U.S. DEPARTMENT OF COMMERCE
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PB-257 706

Utility of Reactivity Criteria in Organic Emission Control Strategies Application to the Los Angeles Atmosphere

TRW/Environmental Services, Redondo Bh, CA

Prepared For
Environmental Sciences Research Lab., Research Triangle Park, N. C.

August 1976

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/3-76-091

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
UTILITY OF REACTIVITY CRITERIA IN ORGANIC EMISSION CONTROL STRATEGIES
Application to the Los Angeles Atmosphere

5. REPORT DATE
August 1976

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
TRW Environmental Services
One Space Park
Redondo Beach, CA 90278

10. PROGRAM ELEMENT NO.
1A1008

11. CONTRACT/GRANT NO.
68-02-1735

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Sciences Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA-ORD

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report investigates the impact of reactivity criteria on organic emission control strategies in the Metropolitan Los Angeles Air Quality Control Region. The investigation involved assembling data on total organic emission rates, on organic emission composition, and on emission reactivity for the Los Angeles basin. On the basis of this data, calculations were then made of the degree to which each emission source type should be controlled to achieve the air quality standard for ozone/oxidant. Results were obtained and compared for the cases of indiscriminate control and of selective, reactivity-based control.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution *Ozone *Organic compounds *Emission *Chemical reactivity *Control *Planning	Los Angeles	13B 07B 07C 07D 05A

PRICES SUBJECT TO CHANGE

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 236
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE $8.00

EPA Form 2220-1 (9-73)

PB 257 706

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA-600/3-76-091
August 1976

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Application to the Los Angeles Atmosphere

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ACKNOWLEDGEMENT

In assembling data on the composition of organic emission sources, TRW Environmental Services received help from numerous people in industry and in governmental agencies. The industries included petroleum refineries, surface coating manufacturers, solvent distributors, diesel manufacturers, aircraft engine producers, and environmental research corporations. Governmental agencies included the Environmental Protection Agency, the Bureau of Mines, and the California Air Resources Board. Particularly helpful support was supplied by several members of the Los Angeles County Air Pollution Control District, especially Sanford Weiss and George Thomas.

TRW gratefully acknowledges the efforts which were made to provide information. TRW takes full responsibility for approximations made in organizing the data and for any errors involved.

ABSTRACT

This report investigates the impact of reactivity criteria on organic control strategies in the Metropolitan Los Angeles AQCR. The investigation involves assembling data on total organic emissions, gathering data on organic composition, computing source reactivities, determining required source emission reductions, and evaluating alternative approaches to organic control policy.

An emission inventory of total organics is assembled from several existing inventories. The resulting inventory is organized into 26 source categories. Composition data are gathered for each source category. These data are tabulated according to 2-group, 5-group, and 6-group reactivity classification schemes provided by the EPA Chemistry and Physics Laboratory.

The composition data are used to determine average molecular weights, reactivities, and reactive emissions for each source category. Results are presented on both a molar basis and a weight basis. The main features of the source reactivity and reactive emission tabulation are discussed.

The overall degree of reactive organic control necessary to achieve the national oxidant standard in Los Angeles is evaluated. Because of high uncertainty in the required degree of control, 90% overall reduction is selected as an arbitrary target level. Individual source emission reductions which attain 90% overall reactive organic control are determined for various reactivity schemes.

The implications of reactivity criteria on organic control policy are discussed. A very approximate assessment is made of the costs and benefits associated with three alternative control approaches, an indiscriminate strategy and two reactivity based strategies.

This report was submitted in fulfillment of Project No. 68-02-1735 by TRW, Inc., under sponsorship of the Environmental Protection Agency. Work was completed as of 15 December 1975.

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TABLE OF CONTENTS

Pages

1.0 INTRODUCTION AND SUMMARY 1-1

1.1 Basic Definitions.................................. 1-2
1.2 Summary of Findings and Conclusions.................. 1-6
1.3 Needs for Future Work.............................. 1-14
1.4 References... 1-16

2.0 A TOTAL ORGANIC EMISSION INVENTORY........................ 2-1

2.1 References... 2-12

3.0 COMPOSITION DATA FOR ORGANIC EMISSION SOURCES.............. 3-1

3.1 Data Policies and Assumptions...................... 3-2

3.1.1 Sources of Composition Data.................. 3-2
3.1.2 Composition Estimates........................ 3-3
3.1.3 Estimation of Average Molecular Weights....... 3-4

3.2 Stationary Sources - Organic Fuels and Combustion.... 3-4

3.2.1 Petroleum Production and Refining............ 3-4
3.2.2 Gasoline Marketing........................... 3-11
3.2.3 Fuel Combustion.............................. 3-17
3.2.4 Waste Burning and Other Fires................ 3-22

3.3 Stationary Sources - Organic Chemicals.............. 3-24

3.3.1 Surface Coatings............................. 3-24
3.3.2 Dry Cleaning................................. 3-30
3.3.3 Degreasing................................... 3-32
3.3.4 Printing..................................... 3-37
3.3.5 Industrial Process Sources................... 3-40

3.4 Mobile Sources..................................... 3-48

3.4.1 Light Duty Gasoline Powered Vehicles.......... 3-51
3.4.2 Heavy Duty Gasoline Powered Vehicles.......... 3-59
3.4.3 Other Types of Gasoline Powered Equipment..... 3-60
3.4.4 Diesel Powered Vehicles...................... 3-66
3.4.5 Aircraft..................................... 3-73

3.5 Data Summary....................................... 3-80

3.6 References... 3-84

4.0 SOURCE REACTIVITY RATINGS AND REACTIVE ORGANIC INVENTORIES 4-1

4.1 Source Molar Reactivities.......................... 4-1

4.2 Source Weight Reactivities......................... 4-4

Preceding page blank

TABLE OF CONTENTS (Continued)

Pages

4.3 Reactive Emissions 4-6

5.0 EMISSION REDUCTION STRATEGIES FOR ORGANIC SOURCES 5-1

5.1 Overall Degree of Reactive Hydrocarbon Control Required for Los Angeles 5-1

5.1.1 Review of Oxidant/Precursor Models 5-3
5.1.2 Conclusions With Respect to Required Emission Reductions 5-20

5.2 Guidelines for Determining Individual Source Emission Reductions 5-22

5.2.1 Economic Efficiency Principles 5-22
5.2.2 Source Emission Reductions in the Absence of Control Cost Information 5-26

5.3 Emission Reductions for Organic Sources in the Metropolitan Los Angeles AQCR 5-29

5.4 References 5-33

6.0 EVALUATION OF ALTERNATIVE APPROACHES TO ORGANIC EMISSION CONTROL 6-1

6.1 Organic Emission Standards Based on Reactivity With No Substitutive Controls 6-1

6.1.1 Benefits of the Reactivity Based Strategy with No Substitutive Controls 6-2
6.1.2 Costs of the Reactivity Based Strategy with No Substitutive Controls 6-3

6.2 Organic Emission Standards Based on Reactivity With Substitutive Controls 6-6

6.2.1 Benefits of the Reactivity Based Strategy With Substitutive Controls 6-6
6.2.2 Costs of the Reactivity Based Strategy With Substitutive Controls 6-9

6.3 Implications of the Benefit/Cost Evaluation 6-10

6.4 References 6-13

APPENDICES

A. COMPUTATION OF AVERAGE SOURCE MOLECULAR WEIGHTS A-1

B. ADDITIONAL SUPPORT DATA FOR COMPOSITION ESTIMATES B-1

LIST OF FIGURES

Figure **Page**

3-1 Change in the Relative Emissions from the Carburetor and Fuel Tank with Ambient Temperature...................... 3-56

3-2 Change in the Relative Emissions from Evaporative Sources and Exhaust Gases with Ambient Temperature......... 3-56

5-1 Upper Limit Curves for Three Stations in the Metropolitan Los Angeles AQCR.............................. 5-5

5-2 Aggregated Upper Limit Curve for the Metropolitan Los Angeles AQCR.. 5-6

5-3 Chevron Research Smog Diagram for August-October in Downtown Los Angeles................. 5-8

5-4 California Air Resources Board Aerometric Results, Relationship Between 6-9 A.M. NO_x, 6-9 A.M. HC, and Max-Hour Oxidant Concentrations at Selected Sites...... 5-11

5-5 Oxidant Air Quality vs. Emissions for Central Los Angeles.. 5-13

5-6 EPA Smog Chamber Analysis of Requirements for Attaining the NAAQS for OX and NO_2......................... 5-15

5-7 Distribution of Morning Precursor Concentrations in Downtown Los Angeles....................................... 5-17

5-8 Los Angeles APCD Diagram of Max Ozone Concentrations vs. Precursor Concentrations............................. 5-19

5-9 Total and Marginal Control Cost Curves for Two Hypothetical Emission Sources 5-24

5-10 Hypothetical Example of Total and Marginal Cost Curves Which Account for Source Reactivity 5-25

LIST OF TABLES

Table		Page
1-1	Five Class Reactivity Categorization of Organic Compounds....	1-3
1-2	Molar Reactivity Ratings for the 2-, 5-, & 6- Group Classification Schemes..............................	1-4
1-3	Organic Emission Inventory for the Metropolitan Los Angeles AQCR..................................	1-7
1-4	Source Organic Composition Data According to the Six Group Classification Scheme...........................	1-9
1-5	Molar Reactivities, Weight Reactivities, and Reactive Emissions...................................	1-10
1-6	Individual Source Emission Reductions for 90% Overall Degree of Control..................................	1-13
2-1	1972 Total Organic Emission Inventory for the Metropolitan Los Angeles AQCR..................................	2-3
3-1	Estimated Composition of the Organic Emissions Due to Petroleum Production	3-6
3-2	Estimated Composition of Organics Emitted by Petroleum Producing Operations	3-7
3-3	Summary of Organic Emissions From Refinery Sources...........	3-9
3-4	Organic Emissions From Each Type of Refinery Source	3-10
3-5	Estimate of the Composition of Organic Refinery Emissions..	3-12
3-6	Estimated Composition of the Organics Emitted From Refinery Operations	3-13
3-7A	Equilibrium Composition of Gasoline Vapors Over Liquid Gasoline	3-15
3-7B	Composition of the Emissions From Underground Gasoline Storage Tanks	3-15
3-8	Composition of Organics Emitted From Underground Gasoline Storage Tanks	3-16
3-9	Equilibrium Vapors Above Liquid Gasoline	3-18

Preceding page blank

LIST OF TABLES (Continued)

Table		Page
3-10	Hydrocarbon Composition of Los Angeles Area Gasolines	3-18
3-11	Composition of Organics Emitted Due to Automobile Gasoline Tank Filling	3-19
3-12	Estimated Composition of the Organics Emitted During Fuel Combustion	3-20
3-13	Composition of the Organics Emitted During Fuel Combustion	3-21
3-14	Estimated Composition of the Organics Emitted Due to Waste Burning and Other Fires	3-22
3-15	Composition of the Organics Emitted by Waste Burning and Other Fires	3-23
3-16	Average Distribution of the Organic Compounds Emitted During Heat Treating of Coatings	3-25
3-17	Approximate Composition of the Organics Emitted During Heat Treating of Surface Coatings	3-26
3-18	Composition of Surface Coating Solvents	3-28
3-19	Composition of the Organics Emitted During Curing of Air Dried Surface Coatings	3-29
3-20	Composition of Petroleum Dry Cleaning Solvents	3-31
3-21	Reactivity Classification for Dry Cleaners Using Petroleum Based Solvent	3-33
3-22	Reactivity Classification for Dry Cleaners Using Synthetic Solvent-(PCE)	3-34
3-23	Organics Emitted by TCE Degreasing Operations	3-35
3-24	Organics Emitted by 1,1,1-T Degreasing Operations	3-36
3-25	Organic Composition Data for Emissions From Rotogravure Printing	3-37
3-26	Estimated Composition of the Organic Compounds Emitted by Rotogravure Printing Operations	3-38
3-27	Estimated Composition of the Organics Emitted by Rotogravure Printing	3-39

LIST OF TABLES (Continued)

Table Page

3-28 Estimated Composition of the Organic Compounds Emitted by Flexigraphic Printing Operations.................. 3-40

3-29 Estimated Composition of the Organics Emitted by Flexigraphic Printing 3-41

3-30 Organic Emission Composition for Rubber, Plastic, Putty, and Adhesive Manufacturing (1965 LA APCD Data)....... 3-42

3-31 Estimated Composition of the Organics Emitted by Rubber, Plastic, Putty and Adhesive Manufacturing Operations........ 3-43

3-32 Estimated Composition of the Organics Emitted During Rubber, Plastic, Putty and Adhesive Manufacturing........... 3-44

3-33. Organic Emission Composition for Pharmaceutical Manufacturing (1965 LA APCD Data)........................... 3-45

3-34 Estimated Composition of the Hydrocarbons in Pharmaceutical Manufacturing................................ 3-46

3-35 Estimated Composition of the Organics Emitted During Pharmaceutical Manufacturing................................ 3-47

3-36 Composition of Organic Emissions From Miscellaneous Organic Solvent Operations................................ 3-48

3-37 Estimated Composition of the Organics Emitted by Miscellaneous Organic Solvent Operations................... 3-49

3-38 Estimated Distribution of the Organics Emitted by Miscellaneous Organic Solvent Operations................... 3-50

3-39 Exhaust Organic Composition for Various Types of Fuel Mixtures.. 3-52

3-40 Exhaust Organic Composition for Various Types of Emission Control Devices................................. 3-53

3-41 Composition of the Organics Emitted in the Exhaust From Light Duty Gasoline Powered Vehicles.................... 3-55

3-42 Ratio of Evaporative to Exhaust Organic Emissions............ 3-58

3-43 Equilibrium Vapors Over Los Angeles Area Gasolines........... 3-58

3-44 Composition of Hydrocarbon Emissions From Automobile Carburetors and Fuel Tanks....................... 3-60

LIST OF TABLES (Continued)

Table | **Page**

3-45 Composition of the Evaporative Emissions From Light Duty Gasoline Powered Vehicles.......... 3-61

3-46 Composition of the Organics Emitted in the Exhaust From Heavy Duty Gasoline Powered Motor Vehicles.......... 3-62

3-47 Composition of the Evaporative Emissions From Heavy Duty Gasoline Powered Vehicles.......... 3-63

3-48 Composition of the Organics Emitted in the Exhaust of Other Types of Gasoline Powered Equipment.......... 3-64

3-49 Composition of the Evaporative Emissions From Other Gasoline Powered Equipment.......... 3-65

3-50 Diesel Engine Exhaust Hydrocarbon Composition.......... 3-67

3-51 Comparison of Diesel Fuel Composition and the Composition of Diesel Exhaust Hydrocarbons.......... 3-70

3-52 Organic Composition of the Exhaust From Diesel Powered Vehicles.......... 3-71

3-53 Comparison of the Organic Emissions From Gasoline and Diesel Powered Vehicles.......... 3-72

3-54 Comparison of the Mass Hydrocarbon Emission Rates From Diesel Powered Vehicles and Gasoline Powered Passenger Cars.......... 3-72

3-55 Fraction of Hydrocarbon Emissions Occurring in Each Operating Mode.......... 3-73

3-56 Distribution of the Organics in Gas Turbine Exhaust.......... 3-74

3-57 Approximate Distribution of Organic Types by Carbon Number Category.......... 3-75

3-58 Variations in the Composition of the Organic Emissions From Gas Turbine (Jet) Aircraft Engines With Power Setting.......... 3-76

3-59 Organic Emissions From Gas Turbine Engines.......... 3-78

3-60 Composition of the Organics Emitted in Piston Aircraft Engine Exhaust (as Approximated by Uncontrolled Automotive Emissions).......... 3-79

3-61 Distribution of Organic Compounds in a 2-Class Reactivity Scheme.......... 3-81

LIST OF TABLES (Continued)

Table		Page
3-62	Distribution of Organic Compounds in a 5-Class Reactivity Scheme	3-82
3-63	Distribution of Organic Compounds in a 6-Class Reactivity Scheme	3-83
4-1	Source Molar Reactivities for the 2-, 5-, and 6-Group Schemes	4-2
4-2	Source Weight Reactivities for the 2-, 5-, and 6-Group Schemes	4-5
4-3	Reactive Emission Inventories for the 2-, 5-, and 6-Group Schemes	4-7
5-1	Estimates of Required Degree of RHC Control for OX Standard Attainment in the Metropolitan Los Angeles AQCR	5-20
5-2	Individual Source Emission Reductions for 90% Overall Degree of Control	5-31
5-3	Individual Source Emission Reductions for Various Degrees of Overall Control (According to the 5-Group Scheme	5-32
6-1	Estimated Costs for Establishing Reactivity Based Organic Emission Regulations	6-5
6-2	The Effect of Substituting Class III Compounds for Class IV and Class V Compounds in Several Selected Source Categories	6-8
6-3	Costs of the Second Reactivity Based Policy	6-11

1.0 INTRODUCTION AND SUMMARY

Organic emission reactivity refers to the potential of an organic to participate in atmospheric reactions which result in photochemical smog. The particular smog symptom of interest here is photochemical oxidant for which a short-term National Ambient Air Quality Standard has been established. Oxidant producing potential is known to vary widely among specific organic compounds. This variation is significant because it introduces the option of selective organic emission control as a possibly advantageous alternative to the less flexible approach of indiscriminate control. However, to date, reactivity criteria have been used by the Environmental Protection Agency and other control agencies in a nonrigorous and inconsistent manner.

Recently, work has been carried out by EPA to develop a more systematic reactivity classification for organic emissions, [1]. This has resulted in a new 5-class reactivity categorization for organics. While a rigorous and consistent application of these criteria would provide a more rational approach to organic control, little is known about the feasibility and real advantages of such an application.

TRW Environmental Services has been contracted by EPA to investigate the impact of reactivity criteria on organic emission control strategies for the Metropolitan Los Angeles Air Quality Control Region. This case study explores the feasibility of using reactivity criteria in organic control and delineates the advantages gained as well as the problems encountered in the approach. This document is the final report for the project.

There are five main objectives in the present study:

- Assemble existing inventory data for total organic emissions in the Metropolitan Los Angeles AQCR for 1972.
- Gather organic composition data for the source types in the inventory and categorize these data according to alternative reactivity classification schemes.

- Compute reactivities for each source type and investigate the sensitivity of these results to alternative reactivity classification schemes.
- Derive required emission reductions (based on reactivity criteria) for organic source categories in the Metropolitan Los Angeles AQCR.
- Evaluate the efficiencies, costs, and problems inherent in alternative approaches to organic emission control.

The five subsequent chapters of this report correspond to the five objectives above. The present chapter includes three more sections. Section 1.1 discusses basic definitions and establishes a consistent terminology for the report. Section 1.2 provides a brief summary of findings and conclusions. Section 1.3 discusses areas where future work is needed.

1.1 BASIC DEFINITIONS

The photochemical reactivity of an organic compound generally refers to the ability of that organic to produce photochemical smog symptoms when it is mixed with nitrogen oxides and irradiated by sunlight. Reactivity can be measured according to a variety of criteria; the principal criteria are organic consumption rate, NO_2 formation rate, oxidant production, and eye irritant production. In this study, reactivity will refer specifically to the potential of organics to produce oxidant/ozone.

Three different reactivity classification schemes will be used herein for deriving reactivity ratings. All three schemes are based on the categorization given in Table 1-1. In the 2-group reactivity classification scheme, all organics in Class I of Table 1-1 are assigned zero reactivity, and all organics in Classes II through V are assigned a reactivity of one. In the 5-group reactivity classification scheme, individual reactivity ratings are assigned to each of the five classes. The 6-group reactivity scheme is the same as the 5-group scheme with the exception that methane is treated individually (as Class 0) and is assigned a zero reactivity.

Table 1-2 summarizes the molar reactivity ratings (or molar reactivities) for the 2-group, 5-group, and 6-group schemes. These ratings are based on the oxidant production potential (per mole) of organics in each class as determined in a recent review of smog chamber data by EPA, [1]. For

TABLE 1-1. FIVE CLASS REACTIVITY CATEGORIZATION OF ORGANIC COMPOUNDS

CLASS I	CLASS II	CLASS III	CLASS IV	CLASS V
C_1-C_3 paraffins	Mono-tert-alkyl benzenes	C_{4+}-paraffins	Prim-& sec-alkyl benzenes	Aliphatic olefins
Acetylene	Cyclic ketones	Cycloparaffins	Dialkyl benzenes	α-methyl styrene
Benzene	Tert-alkyl acetates	Alkyl acetylenes	Branched alkyl ketones	Aliphatic aldehydes
Benzaldehyde	2-nitropropane	Styrene	Prim-& sec-alkyl alcohols	Tri-& tetra-alkyl benzenes
Acetone		N-alkyl ketones	Cellosolve acetate	Unsaturated ketones
Tert-alkyl alcohols		Prim-& sec-alkyl acetates	Partially halogenated olefins	Diacetone alcohol
Phenyl acetate		N-methyl pyrrolidone		Ethers
Methyl benzoate		N,N-dimethyl acetamide		Cellosolves
Ethyl amines				
Dimethyl formamide				
Methanol				
Perhalogenated hydrocarbons				
Partially halogenated paraffins				

convenience in defining various other parameters, the molar reactivities are assigned zero dimensions in this report.

The ratings for the 5- and 6- group schemes are all relative; they have been determined by comparing the relative amounts of oxidant produced by Classes I through V. In this sense, the 5- and 6- group reactivity ratings contain one arbitrary constant, for instance the absolute reactivity rating assigned to Class I. To facilitate comparing the results of using the three different reactivity schemes, the arbitrary constants for the 5- and 6- group schemes have been chosen so that auto exhaust has the same absolute molar reactivity rating as it does in the 2-group scheme. Data for Los Angeles indicate that this rating is .72, (see Chapters 3 and 4).

TABLE 1-2. MOLAR REACTIVITY RATINGS FOR THE 2-, 5-, & 6-GROUP CLASSIFICATION SCHEMES

CLASS	2- GROUP SCHEME	5- GROUP SCHEME	6- GROUP SCHEME
0 (CH_4)	0	.098	0
I	0	.098	.099
II	1	.34	.34
III	1	.64	.64
IV	1	.95	.95
V	1	1.40	1.42

Source molar reactivities can be calculated from the molar reactivity ratings for individual compounds in a straightforward manner. For instance, consider an organic emission source with a composition specified by molar fractions, X_i, for n compounds, i =1, ..., n. The dimensionless source molar reactivity rating for the k-group scheme (SMR^k) is given by

$$SMR^k = \sum_{i=1}^{n} X_i R_i^k , \qquad (1\text{-}1)$$

where R_i^k are the molar reactivity ratings of the individual compounds according to the k-group scheme. For the case of the 2-group scheme, the source molar reactivity is just the fraction of molar emissions that are in Classes II through V.

Since air pollution control strategies are usually formulated using emission inventories which are on a weight basis, it is also useful to express source reactivities per weight. Source weight reactivities should be proportional to reactive moles per unit weight of emissions. Relative source weight reactivities can be derived by just dividing the source molar reactivities by the average molecular weight for each source. Since all reactivities are relative, an arbitrary constant is involved in stating source weight reactivities. Again, we have chosen this constant so that auto exhaust has a rating of .72 for each classification scheme. The appropriate formula for deriving the dimensionless source weight reactivities for each of the k-group schemes (SWR^k) is

$$SWR^k = \frac{MW_{ex} \cdot SMR^k}{MW} \qquad (1-2)$$

where

SMR^k = the source molar reactivity for the source in question,

MW_{ex} = the average molecular weight of auto exhaust,

and MW = the average molecular weight for the source in question.

It should be noted that the source weight reactivity for the 2-group scheme, as calculated by equation (1-2), is not the fraction by weight of reactive organics. The fraction by weight of reactive organics is actually not very meaningful. For instance, assume that two sources each consist entirely of reactive compounds and that the first source has half the molecular weight of the second. The fraction by weight of reactive organics is the same for each source (100%). However, the first source contributes twice as many reactive molecules per ton and should be assigned twice the weight reactivity according to a 2-group scheme. Equation (1-2) would assign that source twice the weight reactivity according to the 2-group scheme.

A reactive emissions inventory can be derived from the source molar (or weight) reactivities and a total hydrocarbon inventory. The moles/day of emissions from each source should be multiplied by the source molar reactivity to obtain the reactive inventory in terms of *reactive moles per day*. Alternatively, the weight/day of emissions from each source can be multiplied by the source weight reactivity to obtain a reactive inventory with units of *reactive weight per day*. The reactive mole inventory and the reactive weight inventory will be directly proportional to one another* That is, each inventory will lead to the same conclusions concerning the relative importance of various sources to oxidant formation.

1.2 SUMMARY OF FINDINGS AND CONCLUSIONS

The major findings and conclusions which have resulted from this study are summarized in the paragraphs that follow. The discussion is organized according to emission inventory of total organics (Chapter 2), composition data for organic sources (Chapter 3), source reactivities and reactive emissions (Chapter 4), required source emission reductions (Chapter 5), and benefits/costs of alternative approaches to organic control (Chapter 6).

Emission Inventory of Total Organics (Chapter 2)

- Table 1-3 presents an inventory of total organic emissions in the Metropolitan Los Angeles AQCR. Weight emissions, molar emissions, and average molecular weights are tabulated for twenty-six source categories. The weight emission estimates represent a combination of data from several existing emission inventories. The estimates of average molecular weights and molar emissions are based on composition data assembled in this study.

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* Proof:

For each source,

$$\text{reactive moles} = (\text{total moles}) \cdot \text{SMR}^k$$

and

$$\begin{aligned}\text{reactive weight} &= (\text{total weight}) \cdot \text{SWR}^k \\ &= (\text{total moles}) \cdot \text{MW} \cdot \frac{\text{MW}_{ex} \cdot \text{SMR}^k}{\text{MW}} \\ &= (\text{total moles}) \cdot \text{MW}_{ex} \cdot \text{SMR}^k \\ &= \text{reactive moles} \cdot \text{MW}_{ex} \\ &= \text{reactive moles} \cdot \text{constant}\end{aligned}$$

TABLE 1-3. ORGANIC EMISSION INVENTORY FOR THE METROPOLITAN LOS ANGELES AQCR

SOURCE CATEGORY	WEIGHT EMISSIONS		MOLAR EMISSIONS		AVERAGE MOLECULAR WEIGHT
	Tons Per Day	Weight % of Total	10^{-6} Ton Moles Per Day	Mole % of Total	
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION					
Petroleum Production and Refining					
Petroleum Production	62	2.3	214	5.9	29
Petroleum Refining	50	1.9	54	1.5	93
Gasoline Marketing					
Underground Service Station Tanks	48	1.8	83	2.3	58
Auto Tank Filling	104	4.0	141	3.9	74
Fuel Combustion	23	0.9	92	2.5	25
Waste Burning & Fires	41	1.6	124	3.4	33
STATIONARY SOURCES: ORGANIC CHEMICALS					
Surface Coating					
Heat Treated	14	0.5	17	0.5	82
Air Dried	129	5.0	148	4.1	87
Dry Cleaning					
Petroleum Based Solvent	16	0.6	13	0.4	125
Synthetic Solvent (PCE)	25	1.0	15	0.4	166
Degreasing					
TCE Solvent	11	0.4	8	0.2	132
1,1,1-T Solvent	96	3.6	71	2.0	134
Printing					
Rotogravure	31	1.2	38	1.0	82
Flexigraphic	15	0.6	26	0.7	57
Industrial Process Sources					
Rubber & Plastic Manf.	42	1.6	58	1.6	73
Pharmaceutical Manf.	16	0.6	21	0.6	75
Miscellaneous Operations	83	3.2	104	2.9	80
MOBILE SOURCES					
Gasoline Powered Vehicles					
Light Duty Vehicles					
Exhaust Emissions	780	30.0	1130	31.2	69
Evaporative Emissions	481	18.5	529	14.6	91
Heavy Duty VEhicles					
Exhaust Emissions	285	10.9	413	11.4	69
Evaporative Emissions	67	2.6	74	2.0	91
Other Gasoline Powered Equipment					
Exhaust Emissions	110	4.2	159	4.4	69
Evaporative Emissions	22	0.8	24	0.7	91
Diesel Powered Motor Vehicles	12	0.5	13	0.4	88
Aircraft					
Jet	20	0.8	17	0.5	121
Piston	22	0.9	39	1.1	56
TOTAL OR WEIGHTED AVERAGE	2600	100%	3620	100%	71.8

- In the Metropolitan Los Angeles AQCR, gasoline powered vehicles account for the majority of total organic emissions, about 67% by weight and about 64% by mole. Light-duty motor vehicles alone account for about 49% of emissions by weight. Transportation sources other than gasoline powered vehicles, stationary source organic fuel processes, and stationary source organic chemical processes contribute 2%, 13%, and 18% of total organic emissions by weight, respectively.

Composition Data for Organic Sources (Chapter 3)

- Table 1-4 summarizes organic composition estimates organized according to the 6-group reactivity classification scheme. Composition data for individual compound types within each of the six reactivity classes are presented in Chapter 3 of this report.

- On a molar basis, about 35 percent of organic emissions in the Los Angeles AQCR fall in Class III of the reactivity categorization scheme. The remainder is roughly equally distributed among classes 0, I, IV, and V. Negligible amounts of Class II compounds are emitted in Los Angeles.

- With a few exceptions (e.g., automotive exhaust and evaporated gasoline), detailed composition data are not available for most sources. The limited nature of existing data requires that approximations be made in describing the organic composition of various sources. The approximations inherent in the composition estimates are discussed in detail in Chapter 3.

- The composition data accumulated for this study are intended as averages for the Metropolitan Los Angeles AQCR and are strictly applicable to that region only. It is not known how representative these composition data may be for other regions. Due to differences in climate, air pollution regulations, petroleum composition, and industrial processes, the composition of organic emissions will vary from region to region.

Source Reactivities and Reactive Emissions (Chapter 4)

- Table 1-5 lists source molar reactivities, source weight reactivities, and reactive emissions for the 26 source categories in the Metropolitan Los Angeles AQCR. Values are given for each of the 2-group, 5-group, and 6-group reactivity classification schemes.

- Source molar reactivities range from .00 to 1.00, .10 to 1.02, and .10 to 1.01 for the 2-, 5-, and 6-group reactivity schemes, respectively. Source weight reactivities range from .00 to .98, .04 to .92, and .04 to .93 for the 2-, 5-, and 6-group schemes, respectively. However, for each classification scheme and for both molar and weight reactivities, about 90% of total emissions fall in the reactivity range of .50 to .95.

TABLE 1-4. SOURCE ORGANIC COMPOSITION DATA ACCORDING TO THE SIX GROUP CLASSIFICATION SCHEME

SOURCE CATEGORY	MOLAR COMPOSITION (PERCENT)					
	CLASS 0	CLASS I	CLASS II	CLASS III	CLASS IV	CLASS V
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION						
Petroleum Production and Refining						
Petroleum Production	64	20	0	16	0	0
Petroleum Refining	7	9	0	67	3	14
Gasoline Marketing						
Underground Service Station Tanks	3	15	0	60	0	22
Auto Tank Filling	0	4	0	80	6	10
Fuel Combustion	76	12	0	3	1	8
Waste Burning & Fires	59	15	0	7	3	16
STATIONARY SOURCES-ORGANIC CHEMICALS						
Surface Coating						
Heat Treated	2	18	0	28	50	2
Air Dried	0	14	0	52	29	5
Dry Cleaning						
Petroleum Based Solvent	0	0	0	94	5	1
Synthetic Solvent (PCE)	0	100	0	0	0	0
Degreasing						
TCE Solvent	0	0	0	0	100	0
1,1,1-T Solvent	0	100	0	0	0	0
Printing						
Rotogravure	0	16	0	61	23	0
Flexigraphic	0	19	0	8	73	0
Industrial Process Sources						
Rubber & Plastic Manf.	0	16	1	24	7	52
Pharmaceutical Manf.	0	34	1	5	60	0
Miscellaneous Operations	0	44	0	29	18	9
MOBILE SOURCES						
Gasoline Powered Vehicles						
Light Duty Vehicles						
Exhaust Emissions	10	18	0	30	19	23
Evaporative Emissions	0	5	0	58	21	16
Heavy Duty Vehicles						
Exhaust Emissions	10	18	0	30	19	23
Evaporative Emissions	0	5	0	58	21	16
Other Gasoline Powered Equipment						
Exhaust Emissions	10	18	0	30	19	23
Evaporative Emissions	0	5	0	58	21	16
Diesel Powered Motor Vehicles	11	2	0	24	6	57
Aircraft						
Jet	2	7	4	38	15	33
Piston	18	16	0	23	10	33
WEIGHTED AVERAGE	13.0	17.2	0.0	35.5	16.6	17.7

TABLE 1-5. MOLAR REACTIVITIES, WEIGHT REACTIVITIES, AND REACTIVE EMISSIONS

SOURCE CATEGORY	SOURCE MOLAR REACTIVITIES			SOURCE WEIGHT REACTIVITIES			REACTIVE EMISSIONS					
							REACTIVE TONS/DAY			PERCENT OF TOTAL		
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION												
Petroleum Production and Refining												
Petroleum Production	.16	.10	.10	.50	.05	.09	24	30	18	1.4	1.7	1.1
Petroleum Refining	.80	.71	.71	.66	.53	.53	33	27	27	1.9	1.6	1.6
Gasoline Marketing												
Underground Service Station Tanks	.40	.71	.71	.90	.84	.85	47	40	40	2.7	2.4	2.4
Auto Tank Filling	.95	.79	.79	.90	.73	.74	90	76	77	5.4	4.6	4.7
Fuel Combustion	.10	.20	.12	.05	.55	.33	6	13	8	0.3	0.8	0.5
Waste Burning & Fires	.26	.37	.32	.64	.77	.67	22	32	27	1.3	1.9	1.6
STATIONARY SOURCES–ORGANIC CHEMICALS												
Surface Coating												
Heat Treated	.80	.70	.79	.67	.90	.60	9	8	8	0.5	0.5	0.5
Air Dried	.90	.60	.59	.60	.58	.58	88	71	71	5.0	4.3	4.3
Dry Cleaning												
Petroleum Based Solvent	1.00	.66	.60	.55	.36	.36	9	6	6	0.5	0.4	0.4
Synthetic Solvent (PCE)	.90	.10	.10	.08	.04	.04	8	1	1	0.5	0.1	0.1
Degreasing												
TCE Solvent	1.00	.95	.95	.52	.90	.80	6	5	5	0.3	0.3	0.3
1,1,1-T Solvent	.00	.10	.10	.00	.00	.05	0	5	5	0.0	0.3	0.3
Printing												
Rotogravure	.60	.62	.62	.60	.52	.52	21	16	16	1.2	1.0	1.0
Flexographic	.81	.76	.76	.98	.92	.95	15	14	14	0.9	0.8	0.9
Industrial Process Sources												
Rubber & Plastic Manf.	.89	.97	.88	.75	.92	.83	33	31	39	1.9	2.3	2.4
Pharmaceutical Manf.	.65	.64	.64	.61	.50	.59	10	9	9	0.6	0.5	0.5
Miscellaneous Operations	.90	.53	.53	.45	.46	.45	40	36	36	2.3	2.3	2.3
MOBILE SOURCES												
Gasoline Powered Vehicles												
Light Duty Vehicles												
Exhaust Emissions	.72	.72	.72	.72	.72	.72	552	552	552	30.1	33.9	34.2
Evaporative Emissions	.96	.80	.80	.72	.61	.61	340	293	293	19.0	17.7	17.9
Heavy Duty Vehicles												
Exhaust Emissions	.72	.72	.72	.72	.72	.72	205	205	205	11.7	12.3	12.5
Evaporative Emissions	.90	.80	.80	.72	.61	.61	48	41	41	2.7	2.5	2.5
Other Gasoline Powered Equipment												
Exhaust Emissions	.72	.72	.72	.72	.72	.72	79	79	79	4.5	4.8	4.8
Evaporative Emissions	.95	.80	.80	.72	.61	.61	16	13	13	0.9	0.8	0.8
Diesel Powered Motor Vehicles	.67	1.08	1.01	.67	.79	.79	8	9	9	0.5	0.5	0.5
Aircraft												
Jet	.91	.80	.80	.92	.50	.50	10	10	10	0.6	0.6	0.6
Piston	.60	.74	.72	.81	.91	.89	18	20	20	1.0	1.2	1.2
	.70	.66	.66	.67	.64	.63	1749	1668	1641	100%	100%	100%

- There is a significant change in relative source reactivities in going from the 2-group scheme to the 5-group scheme. However, reactivities according to the 5-group and 6-group schemes are nearly identical for most sources. The only notable differences between the 5-group and 6-group schemes involve the source categories of petroleum production, fuel combustion, and waste burning & fires. Methane is a significant fraction of the emissions from each of these three source categories.

- The impact of using reactivity criteria to compute relative source contributions is less than dramatic. Generally, the total organic inventory is similar to each of the three reactive inventories. The only substantial differences occur among relatively minor source types such as petroleum production, underground service station tanks, fuel combustion, PCE dry cleaning solvent, 1,1,1-T degreasing solvent, and rubber & plastic manufacturing.

- According to all three reactivity classification schemes, mobile sources account for three-fourths of reactive emissions in the Metropolitan Los Angeles AQCR. The remaining one-fourth of reactive emissions is about equally divided between stationary source organic fuel processes and stationary source organic chemical processes. Gasoline powered vehicles account for about 72% of reactive emissions, while light-duty vehicles alone contribute 52% of reactive emissions.

Required Source Emission Reductions (Chapter 5)

- The determination of required emission reductions for various source categories requires two inputs. The first is the overall degree of reactive organic emission control necessary to achieve the national air quality standard for oxidant in the Metropolitan Los Angeles AQCR. The second is a set of quidelines for allocating emission reductions to individual source categories.

- A great deal of uncertainty surrounds the degree of reactive organic control that is required to attain the national oxidant standard in the Los Angeles region. A review of four empirical/aerometric models and two smog chamber models indicates that at least 90%, and possibly much higher, control will be necessary. If background hydrocarbon contributions are accounted for, it appears that even 100% control of man-made sources may not be sufficient. This report does not derive source emission reductions aimed at actual attainment of the oxidant standard; rather, 90% overall reactive organic control of man-made sources is selected as a target level for illustrative purposes.

- Economic efficiency principles provide the most appropriate guidelines for allocating emission reductions among individual source categories in order to attain a given overall degree of control. Application of economic efficiency criteria requires detailed data on emission reduction costs for all source categories. Since these cost data are unavailable for most source types, equity guidelines rather than economic guidelines are used in this report to allocate emission reductions among individual sources.

- Table 1-6 lists individual source emission reductions which achieve 90% overall control of reactive organics in the Los Angeles region. These are listed for indiscriminate control as well as for control allocated according to the 2-group, 5-group, and 6-group reactivity schemes. For the reactivity based strategies, control is allocated so that the allowable emissions from each source category are inversely proportional to the reactivity of that category. Accordingly, the sources of highest reactivity are assigned the greatest degree of control with the reactivity based strategies. Two organic sources with extremely low reactivity, PCE dry cleaning and 1,1,1-T degreasing, are actually allowed increased emissions by the reactivity based strategies. Control requirements for all other sources are quite stringent, with nearly all reductions ranging from 80% to 93%.

Benefits/Costs of Alternative Approaches to Organic Control (Chapter 6)

- The first reactivity based control policy evaluated in this report involves establishing emission standards based on present source reactivities but not allowing substitutive controls (replacement of highly reactive constituents with compounds of lower reactivity). Generally, this policy should yield the benefit (over indiscriminate control) of allowing more organic emissions by concentrating emission reductions among the most reactive sources. However, for Los Angeles, the only net benefit of this reactivity based policy is not having to control PCE dry cleaning and 1,1,1-T degreasing. The extra annualized cost (over an indiscriminate control policy) for implementing and administrating this reactivity based policy in Los Angeles would be around $10,000 to $100,000 per year.

- The second reactivity based policy evaluated here establishes emission standards based on reactivity and permits substitutive controls as well as emission reduction controls. The extra benefit of this policy (as compared to the first reactivity based policy) consists of increased flexibility in selecting among alternative control measures. Substitutive control alternatives would be particularly important when replacement can be made with Class 0 or Class I compounds. This usually would involve switches to synthetic solvents or conversion to gaseous fuels (e.g. methane or methanol). Substitution of one petroleum based product for another usually would involve compounds in Classes III to V and generally would not yield substantial reductions in reactivity. The extra annualized cost (over the first reactive policy) of implementing and administrating this second reactivity based policy in Los Angeles would be around $100,000 to $250,000 per year.

TABLE 1-6. INDIVIDUAL SOURCE EMISSION REDUCTIONS FOR 90% OVERALL DEGREE OF CONTROL

SOURCE CATEGORY	PERCENT REDUCTIONS (90% OVERALL DEGREE OF CONTROL)			
	INDISCRIMINATE	2-GROUP SCHEME*	5-GROUP SCHEME*	6-GROUP SCHEME*
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION				
Petroleum Production and Refining				
Petroleum Production	90%	85%	75%	79%
Petroleum Refining	90%	90%	80%	90%
Gasoline Marketing				
Underground Service Station Tanks	90%	94%	92%	92%
Auto Tank Filling	90%	92%	91%	91%
Fuel Combustion	90%	74%	87%	83%
Waste Burning & Fires	90%	86%	93%	90%
STATIONARY SOURCES: ORGANIC CHEMICALS				
Surface Coating				
Heat Treated	90%	93%	88%	93%
Air Dried	90%	90%	88%	88%
Dry Cleaning				
Petroleum Based Solvent	90%	87%	87%	91%
Synthetic Solvent (PCE)	90%	**	-83%	-96%
Degreasing				
TCE Solvent	90%	91%	91%	91%
1,1,1-T Solvent	90%	**	-88%	-88%
Printing				
Rotogravure	90%	90%	91%	87%
Flexigraphic	90%	93%	93%	93%
Industrial Process Sources				
Rubber & Plastic Manf.	90%	90%	93%	93%
Pharmaceutical Manf.	90%	87%	87%	87%
Miscellaneous Operations	90%	88%	88%	87%
MOBILE SOURCES				
Gasoline Powered Vehicles				
Light Duty Vehicles				
Exhaust Emissions	90%	91%	91%	91%
Evaporative Emissions	90%	91%	90%	90%
Heavy Duty Vehicles				
Exhaust Emissions	90%	91%	91%	91%
Evaporative Emissions	90%	91%	93%	90%
Other Gasoline Powered Equipment				
Exhaust Emissions	90%	91%	91%	91%
Evaporative Emissions	90%	91%	91%	91%
Diesel Powered Motor Vehicles	90%	92%	92%	92%
Aircraft				
Jet	90%	88%	88%	88%
Piston	90%	91%	91%	91%
WEIGHTED AVERAGE	90%	--	84.3%	86.4%

* Calculated according to equation (5-6)

** Equation (5-6) assigns infinite allowable emissions in this case

- Based on a very brief evaluation of alternative approaches to organic control, the following approach seems appropriate. An organic control strategy in Los Angeles should require large reductions in emissions from nearly all source categories. Variations in degree of control among most source categories should be based on technical feasibility considerations rather than reactivity considerations. Exceptions should be made only for source categories of extremely low reactivity. PCE dry cleaning and 1,1,1-T degreasing now qualify as exceptions according to the reactivity schemes used here. Other source categories may also qualify in the future; these future exceptions are most likely to involve sources which are converted to synthetic solvents or gaseous fuels.

1.3 NEEDS FOR FUTURE WORK

The present study is subject to several important limitations. Some of these are a direct result of limitations in the available data. This study is based on existing data concerning the amount, composition, and reactivity of organic emission from various source categories in Los Angeles. Often, these data are lacking in detail. In a few cases, the data represent measurements taken more than a decade ago and thus are of uncertain applicability to present emissions in Los Angeles. Other limitations involve the depth of analysis that has been afforded certain issues. Because of the restricted level of effort allocated to this study, some areas (e.g. the costs of individual source emission reductions or the feasibility of substitutive controls) could not be treated in a comprehensive manner. In light of these limitations, it is useful to examine areas where future work can provide supplements and improvements to the present study.

The total organic emission inventory is one area with potential fuel improvement. A comprehensive organic emission inventory project would allow greater confidence to be placed in the emission estimates. A source testing program should be included in such a project. The spatial and temporal distribution of emissions should be determined as well as average emission rates. The emission inventory should be projected into the future to determine changes in the relative importance of various sources as present control policy takes affect.

The composition data for both mobile and stationary sources should be verified. Composition tests could be conducted as part of the source testing program in an emission inventory project.

It would be interesting to apply more alternative oxidant reactivity classification schemes to the composition data presented in this report or to updated composition data as they become available. For instance, various new 2-group classifications or a 3-group classification might be tried. A sensitivity analysis should be performed with these reactivity classifications. The present study provides preliminary evidence that the overall structures of reactive organic inventories are generally insensitive to alternative choices of reactivity classification schemes. It would be useful to determine if this result holds for reactivity classifications other than the 2-, 5-, and 6- group schemes used here.

For use in formulating control strategies for suspended particulate matter, a reactivity classification scheme should be derived based on organic aerosol formation. Once an aerosol reactivity classification is available, it can be applied to the composition data gathered here in a straightforward manner.

This study uses equity guidelines to allocate emission reductions among various source categories in order to attain given overall control. Economic guidelines would be more appropriate, but emission reduction costs must be known for all source categories in order to use the economic criteria. It would be useful to compile data on emission reduction costs for each source category so that individual source emission reductions could be based on cost considerations as well as reactivity considerations. It may very well be that source-to-source variations in control costs are more significant than source-to-source variations in reactivity.

The potential benefits from substitutive control alternatives are given only cursory treatment in this report. More detailed study is needed to quantify these benefits. A comprehensive analysis should include a technological assessment of substitutive control options for each individual source category.

Although further research work is necessary to provide a sound basis for organic control policy, it must be recognized that many policy decisions must be made now or in the near future if significant air quality improvements are to be obtained in this decade. Although the scope of this study needs to be expanded by future work and although the data base needs improvement, this study in its present form can help to guide current policy. For instance, the relative uniformity of reactivity ratings among most source categories indicates that it is important to develop controls for nearly all significant source categories.

1.4 REFERENCES

1. B. Dimitriades, "The Concept of Reactivity and Its Possible Applications In Control", Proceedings of the Solvent Reactivity Converence, EPA-650/3-74-010, November 1974.

2.0 A TOTAL ORGANIC EMISSION INVENTORY

The main thrust of the present project is to use Los Angeles as a case study for assembling organic composition data, computing reactivity factors, investigating the sensitivity of organic emission standards to alternative reactivity schemes, and assessing the consequences of reactivity criteria to control policy. The latter two tasks require a total organic emission inventory as an input. This chapter presents the required total organic inventory for the Metropolitan Los Angeles AQCR.

The demands made on the overall resources of this project by other aspects of this study (e.g. the gathering of organic composition data) ruled out allocating time and effort to produce new information on total organic emissions from various sources. Rather, the total organic emission data were assembled from existing inventories. The main sources of inventory data that were reviewed are as follows:

- The preliminary version of a 1972 inventory being compiled by the California Air Resources Board, [1] (this inventory relies on information from the county Air Pollution Control District for stationary sources. It will subsequently be referred to as the 1972 ARB/APCD inventory.)
- The 1972 National Emission Data System Report (NEDS), [2].
- Detailed stationary source information available for Los Angeles County from the Los Angeles County APCD, [3].
- An inventory of vehicular emissions from an automotive study now in progress at the Jet Propulsion Laboratory (JPL), [4].

Previous TRW experience with emission inventories for the Los Angeles AQCR indicates that the county Air Pollution Control Districts provide the most reliable information on stationary emission sources. The principal function of the county APCD's is to control stationary source emissions. To this end, the Los Angeles County APCD maintains a separate full-time staff responsible for the inventory and control of each source sub-category. On the other hand, it has been our experience that NEDS data for stationary sources in Los Angeles are often in notable error, [5]. Thus, the 1972 ARB/APCD inventory and more detailed data available from the Los Angeles County APCD were relied upon for the stationary source emission estimates.

For mobile sources, data are used from both the 1972 ARB/APCD inventory and the JPL study. However, the JPL results have been given a greater emphasis. This is particularly important for evaporative emission estimates because the JPL study has included recent data which indicate that the new car evaporative controls are operating at low efficiencies.

Table 2-1 presents the total organic emission inventory that will be employed in the present study. Table 2-1a is in English units, while Table 2-1b is in metric units. The inventory is given in weight emissions as well as in molar emissions. The conversion factors (average molecular weights) which have been used to derive molar emissions are also listed. The molecular weights have been derived from the composition data presented in Chapter 3. Appendix A summarizes the molecular weight calculations.

The details on the assumptions used to obtain the total organic emission inventory are listed for each individual source category below:

Petroleum Production

Petroleum production refers to the process of removing oil and gas from the ground. Organic emissions from petroleum production occur primarily from an operation which separates water, gases, and oil at the drill site, [6].

The 1972 ARB/APCD inventory lists 62 tons per day of total organics resulting from petroleum production in the Metropolitan Los Angeles AQCR. This figure disagrees with previous ARB/APCD estimates in 1970 which indicated about 115 tons per day. The 1972 value reflects new information obtained by the LA APCD and ARB on petroleum production sources, and this later estimate is considered more reliable, [7]. The 62 tons per day figure will be used in this study.

Petroleum Refining

Organic emissions result from a variety of processes in petroleum refineries. The main processes included in the refining category (as defined here) are storage, pumping, compression, separation, cooling, and equipment maintenance. Organic emissions from boilers/heaters and surface coating in refineries are included in the fuel combustion and surface coating categories of the emission inventory.

TABLE 2-1. 1972 TOTAL ORGANIC EMISSION INVENTORY FOR THE METROPOLITAN LOS ANGELES AQCR (English Units)

SOURCE CATEGORY	WEIGHT EMISSIONS (TONS/DAY)	% OF TOTAL	MOLAR EMISSIONS (10^{-4} TON MOLES/DAY)	% OF TOTAL	AVERAGE MOLECULAR WEIGHT
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION					
Petroleum Production and Refining					
Petroleum Production	62	2.4	214	5.9	29
Petroleum Refining	50	1.9	54	1.5	93
Gasoline Marketing					
Underground Service Station Tanks	48	1.8	83	2.3	58
Auto Tank Filling	104	4.0	141	3.9	74
Fuel Combustion	23	0.9	92	2.5	25
Waste Burning & Fires	41	1.6	124	3.4	33
STATIONARY SOURCES-ORGANIC CHEMICALS					
Surface Coating					
Heat Treated	14	0.5	17	0.5	82
Air Dried	129	5.0	148	4.1	87
Dry Cleaning					
Petroleum Based Solvent	16	0.6	13	0.4	126
Synthetic Solvent (PCE)	25	1.0	15	0.4	166
Degreasing					
TCE Solvent	11	0.4	8	0.2	132
1,1,1-T Solvent	95	3.6	71	2.0	134
Printing					
Rotogravure	31	1.2	38	1.0	82
Flexigraphic	15	0.6	26	0.7	57
Industrial Process Sources					
Rubber & Plastic Manf.	42	1.6	58	1.6	73
Pharmaceutical Manf.	16	0.6	21	0.6	75
Miscellaneous Operations	83	3.2	104	2.9	80
MOBILE SOURCES					
Gasoline Powered Vehicles					
Light Duty Vehicles					
Exhaust Emissions	780	30.0	1130	31.2	69
Evaporative Emissions	481	19.5	529	14.6	91
Heavy Duty Vehicles					
Exhaust Emissions	285	10.9	413	11.4	69
Evaporative Emissions	67	2.6	74	2.0	91
Other Gasoline Powered Equipment					
Exhaust Emissions	110	4.2	159	4.4	69
Evaporative Emissions	22	0.8	24	0.7	91
Diesel Powered Motor Vehicles	12	0.5	13	0.4	89
Aircraft					
Jet	20	0.8	17	0.5	121
Piston	22	0.8	39	1.1	56
TOTAL	2604	100%	3626	100%	71.9 (Weighted Average)

TABLE 2-1. 1972 TOTAL ORGANIC EMISSION (continued) INVENTORY FOR THE METROPOLITAN LOS ANGELES AQCR (Metric Units)

SOURCE CATEGORY	WEIGHT EMISSIONS (METRIC TONS/DAY)	% OF TOTAL	MOLAR EMISSIONS (10^{-3} METRIC TONS MOLES/DAY)	% OF TOTAL	AVERAGE MOLECULAR WEIGHT
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION					
Petroleum Production and Refining					
Petroleum Production	56	2.4	194	5.9	29
Petroleum Refining	45	1.9	49	1.5	93
Gasoline Marketing					
Underground Service Station Tanks	44	1.9	75	2.3	58
Auto Tank Filling	94	4.0	128	3.9	74
Fuel Combustion	21	0.9	83	2.5	25
Waste Burning & Fires	37	1.6	112	3.4	33
STATIONARY SOURCES-ORGANIC CHEMICALS					
Surface Coating					
Heat Treated	13	0.6	15	0.5	82
Air Dried	117	5.0	134	4.1	87
Dry Cleaning					
Petroleum Based Solvent	15	0.6	12	0.4	126
Synthetic Solvent (PCE)	23	1.0	14	0.4	166
Degreasing					
TCE Solvent	10	0.4	7	0.2	132
1,1,1-T Solvent	86	3.6	64	1.9	134
Printing					
Rotogravure	28	1.2	34	1.0	82
Flexigraphic	14	0.6	24	0.7	57
Industrial Process Sources					
Rubber & Plastic Manf.	38	1.6	53	1.6	73
Pharmaceutical Manf.	15	0.6	19	0.6	75
Miscellaneous Operations	75	3.2	94	2.9	80
MOBILE SOURCES					
Gasoline Powered Vehicles					
Light Duty Vehicles					
Exhaust Emissions	707	29.9	1025	31.2	69
Evaporative Emissions	436	18.5	480	14.6	91
Heavy Duty Vehicles					
Exhaust Emissions	258	10.9	375	11.4	69
Evaporative Emissions	61	2.6	67	2.0	91
Other Gasoline Powered Equipment					
Exhaust Emissions	100	4.2	144	4.4	69
Evaporative Emissions	20	0.8	22	0.7	91
Diesel Powered Motor Vehicles					
Aircraft					
Jet	18	0.8	16	0.5	181
Piston	20	0.8	35	1.1	56
TOTAL	2362	100%	3286	100%	71.9 (Weighted Average)

The 1972 ARB/APCD inventory indicates that 50 tons per day of organic emissions result from petroleum refining in the Metropolitan Los Angeles AQCR. This value will be used here. A breakdown of these emissions among the various refining processes is given later in Table 3-3 .

Gasoline Marketing: Underground Service Station Tanks

Underground storage tanks at service stations are a source of organic emissions when the gasoline vapor is displaced into the atmosphere as the tanks are refilled. These tanks also emit some organics through a "breathing" process caused by the diurnal cycle in ground temperature.

The 1972 ARB/APCD inventory lists 152 tons per day of organic emissions from gasoline marketing. This includes emissions from both underground service station tanks and the filling of automobile tanks. Los Angeles APCD data indicate that 31.8% of this total is from the underground tanks. Thus, a value of 48 tons per day will be used for HC emissions from underground tanks.

Gasoline Marketing: Automobile Tank Filling

During automobile tank filling, organic emissions occur because the gasoline vapor in the automobile tank is displaced into the atmosphere. Some emissions (about a fifth of the total for this category) also result from spillage. Using the ARB/APCD data as in the underground tank category above, a value of 104 tons per day is obtained for the organic emissions from auto tank filling in the Metropolitan Los Angeles AQCR.

Fuel Combustion

This category includes organic emissions from the combustion of fuel oil, natural gas, and refinery make gas. The 1972 ARB/APCD inventory indicates that 23 tons per day of organic emissions result from fuel combustion, (power plants-34%, industry-35%, domestic/commercial-8%, and orchard heaters-23%).

Waste Burning and Fires

The 1972 ARB/APCD inventory lists 41 tons per day of organic emissions from waste burning and fires in the Metropolitan Los Angeles AQCR. These emissions result from structural fires (66%), wild fires (18%), agricultural burning (9%), and other burning (7%).

Surface Coating: Heat Treated

The heat treated surface coating category includes organic emissions from processes where the organic solvent comes in contact with flame or is baked, heat-cured or heat-polymerized in the presence of oxygen, [8]. Los Angeles APCD data indicate that about 10% of surface coating emissions are heat-treated.

The 1972 ARB/APCD inventory lists 112 tons per day of organics from all surface coating operations in the Metropolitan Los Angeles AQCR. Recent data for 1972 obtained from the Los Angeles APCD list 121 tons per day for Los Angeles County alone,* [3]. The nature of this disagreement is not known. For the present study, it was decided to adjust the 1972 ARB/APCD inventory to reflect the Los Angeles APCD results. Accordingly, total organics from surface coating will be taken as 143 tons per day in the Los Angeles AQCR. Since approximately 10% of this total is heat-treated [3], the emissions from heat-treated surface coatings amount to 14 tons per day.

Surface Coating: Air Dried

Air dryed surface coating emissions in the Metropolitan Los Angeles AQCR result mostly from industrial paint spray booths and architectural painting. Of the 143 tons per day of total surface coating emissions in the Los Angeles AQCR, approximately 90% is from air dryed processes, (see above paragraph). Thus, air dryed coating emissions amount to 129 tons per day.

Dry Cleaning: Synthetic Solvent (PCE)

There are basically two types of solvents used in dry cleaning operations in the Metropolitan Los Angeles AQCR. These are synthetic solvent (perchloroethylene) and petroleum based solvent. The 1972 ARB/APCD inventory lists 17.5 tons per day for total dry cleaning emissions. This figure does not agree with recent Los Angeles APCD data for 1972 which indicate 33.5 tons per day for Los Angeles County alone,** [3]. For the present study, it was decided to adjust the 1972 ARB/APCD inventory to reflect the Los Angeles APCD results. Accordingly, the total organic emissions from all dry cleaning operations in the Los Angeles AQCR will be taken as 41 tons per day.

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[*] The 1972 ARB/APCD inventory lists 90 tons per day from Los Angeles County.

[**] The 1972 ARB/APCD inventory lists 10 tons per day from Los Angeles County.

Los Angeles APCD data indicate that 63% of dry cleaning emissions in the County are from synthetic solvent users. Calculations with the 1972 ARB/APCD inventory indicate that 57% of the dry cleaning emissions in the basin are from synthetic solvent use.* These percentages are in good agreement; here, it will be assumed that 60% of dry cleaning emissions are from synthetic solvent (PCE). Thus, 25 tons per day of organic emissions arise from dry cleaners using synthetic solvents in the Metropolitan Los Angeles AQCR.

Dry Cleaning: Petroleum Based Solvent

Of the 41 tons per day of organic emissions from dry cleaning, about 40% come from cleaning plants using petroleum based solvent, (see previous section). Thus, petroleum based solvent emissions from dry cleaning amount to 16 tons per day.

Degreasing: TCE Solvent

There are basically two types of organic solvents used for degreasing operations in the Metropolitan Los Angeles AQCR: trichloroethylene (TCE) and 1,1,1,-trichloroethane (1,1,1,-T). The 1972 ARB/APCD inventory lists 92 tons per day for the total emissions from degreasing in the Los Angeles AQCR. This figure disagrees with recent Los Angeles APCD data for 1972 which indicate 94 tons per day for Los Angeles County alone,**[3]. Altering the 1972 ARB/APCD results to reflect the Los Angeles APCD data, we obtain 106 tons per day as the total organic emissions from degreasing in the AQCR.

The 1972 ARB/APCD inventory indicates 11 tons per day of "reactive" solvent from degreasing in the AQCR. According to the ARB/APCD definition of reactivity, this represents TCE solvent. Recent Los Angeles APCD data is consistent with this estimate; we will use the 11 tons per day figure for TCE degreasing emissions.

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* These calculations assume that the ARB has assigned a 20% reactivity factor to petroleum type solvent in computing reactive hydrocarbon contributions.

** The 1972 ARB/APCD inventory lists 80 tons per day for Los Angeles County alone.

Degreasing: 1,1,1-T Solvent

Total degreasing emissions, minus TCE emissions, essentially consist of 1,1,1-T emissions. Thus, using the data presented in the above section, we obtain an estimate of 95 tons per day of organic emissions from 1,1,1-T degreasing in the Los Angeles AQCR.

Printing: Rotogravure

Information on emissions from rotogravure printing are not available for the entire Los Angeles AQCR. Recent Los Angeles APCD data indicate 29.5 tons per day from rotogravure printing in Los Angeles County in 1972, [3]. To obtain a basinwide estimate, this value will be multiplied by 1.04 which is the ratio of AQCR "miscellaneous organic solvent emissions" to Los Angeles County "miscellaneous organic solvent emissions" indicated by the 1972 ARB/APCD inventory. Thus, a value of 31 tons per day will be used for organic emissions from rotogravure printing in the entire AQCR.

Printing: Flexigraphic

Information on organic emissions from flexigraphic printing are available only for the Los Angeles County portion of the AQCR. Recent Los Angeles APCD data list 14.5 tons per day for 1972, [3]. To obtain a basinwide estimate, this value will be multiplied by 1.04 (see above section). Thus, 15 tons per day represents the emissions from flexigraphic printing in the entire Los Angeles AQCR.

Rubber, Plastic, Adhesive, and Putty Manufacturing

Los Angeles County APCD data for 1972 list 40 tons per day of organic emissions from rubber, plastic, adhesive, and putty manufacturing, [3]. Data are not available basinwide for this category. To obtain an estimate for the entire AQCR, the Los Angeles County emissions are multiplied by 1.04 (see discussion under rotogravure printing). Thus, 42 tons per day is the emission estimate for the Los Angeles AQCR.

Pharmaceutical Manufacturing

The manufacture of drugs and cosmetics resulted in 15 tons per day of organic solvent emissions in Los Angeles County in 1972, [3]. A basinwide estimate of 16 tons per day is obtained employing procedures similar to those used for rotogravure printing (see above).

Miscellaneous Organic Solvent Operations

The present category consists of miscellaneous chemical manufacturing (e.g. soaps, cleaners, insecticides, fertilizers, explosives, etc.) as well as miscellaneous solvent usage in industry (e.g. the potting of electrical and electronic equipment). Information is not available for the entire AQCR on organic emissions from this category. Los Angeles APCD data for 1972 indicate 80 tons per day of miscellaneous organic solvent emissions in Los Angeles County alone. This is factored by 1.04 (see above) to yield an estimate of 83 tons per day for the entire Los Angeles AQCR.

Light Duty Motor Vehicles: Exhaust Emissions

Light duty motor vehicles (LDMV's) include gasoline powered automobiles and trucks which are less than 6000 lb. gross weight. The recent automotive system study at the Jet Propulsion Laboratory concluded that approximately 780 tons per day of exhaust organic emissions resulted from LDMV's in the Metropolitan Los Angeles Region in 1972. [4]. The JPL study included a review of available information on automotive use patterns in the Los Angeles AQCR. This review provided data on total vehicle miles travelled as well as on the vehicle age distribution and the age/mileage distribution. The JPL study used measured emission factors, speed correction factors, and deterioration factors as published in the 1973 version of EPA AP-42, [9].

The result obtained by JPL differs somewhat from the 1972 ARB/APCD inventory which lists 931 tons per day from LDMV exhaust in the Los Angeles AQCR. The nature of this disagreement is not known. The present study will use the JPL estimate of 780 tons per day.

Light Duty Motor Vehicles: Evaporative Emissions

Based on recently published automotive test data, the JPL study concluded that about 481 tons per day of evaporative organic emissions resulted from LDMV's in the Los Angeles AQCR in 1972, [4], [10], [11]. This figure is much greater than the 248 tons per day listed in the 1972 ARB/APCD inventory as evaporative emissions from all gasoline powered vehicles. Part of this disagreement is probably due to the test data emission factors which JPL used. For instance, these data indicate that the new car evaporative controls have only about a 30% control efficiency,

[3]. A more minor source of disagreement is that the JPL study incorporates crankcase emissions in the evaporative category. The Los Angeles APCD inventory for 1971 generally agrees with the JPL results rather than the 1972 ARB/APCD results. The present study will use the JPL estimate of 481 tons per day.

Heavy Duty Motor Vehicles: Exhaust Emissions

The JPL study used recent data on HDMV population, usage, and emission factors to derive that 285 tons per day of exhaust organic emissions resulted from gasoline powered HDMV's in the Los Angeles AQCR in 1972. This estimate agrees quite well with the 1972 ARB/APCD inventory which lists 309 tons per day for HDMV exhaust emissions. The JPL result will be used in the present study.

Heavy Duty Motor Vehicles: Evaporative Emissions

The JPL automotive study concluded that 67 tons per day of evaporative and crankcase emissions resulted from HDMV's in the Los Angeles AQCR in 1972. This figure will be used in the present study.

Other Gasoline Powered Equipment: Exhaust Emissions

The 1972 ARB/APCD inventory listed 110 tons per day of organic exhaust emissions from other gasoline powered equipment. This includes motorcycles (27 tons/day), other off-road vehicles (61 tons/day), and commercial & residential utility equipment (22 tons/day). The motorcycle emission estimates agree quite well with the results of the JPL study which indicated 31 tons/day for motorcycles. Other studies are not available for comparison with the ARB/APCD results for off-road vehicles and commercial & residential utility equipment. The 110 tons per day figure will be used here for exhaust emissions from the other gasoline powered equipment category.

Other Gasoline Powered Equipment: Evaporative Emissions

Published information is not available for evaporative emissions for this entire category. The JPL study indicated that evaporative and crankcase emissions from motorcycles were 10% of exhaust emissions in 1972. However, one would expect that other off-road vehicles might yield evaporative and crankcase emissions as high as 30% of exhaust emissions, (i.e., similar to uncontrolled automobiles). Here, it will be assumed that evaporative and crankcase emissions from the "other gasoline powered equipment" category amount to 20% of the exhaust emissions for that category. Thus, 22 tons per day of organic emissions will be used for evaporation and crankcase emissions from other gasoline powered equipment in the Los Angeles AQCR in 1972.

Diesel Powered Motor Vehicles

The JPL study used National Bureau of Highway estimates for diesel usage in urban areas and EPA emission factors to derive that 12 tons per day of organic emissions result from diesel motor vehicles in the Los Angeles AQCR in 1972. These emissions are nearly all from diesel exhaust; evaporative emissions are negligible and crankcase blowby has been controlled. The JPL result is much lower than the 1972 ARB/APCD inventory which lists 32 tons per day of organics from diesel exhaust. However, both the 1971 Los Angeles APCD inventory and the EPA NEDS inventory tend to confirm the JPL estimate. Diesel powered motor vehicle emissions of organics will be taken as 12 tons per day in the present study.

Jet Aircraft

The 1972 ARB/APCD inventory indicates that 20 tons per day of orgainc emissions resulted from jet aircraft in the Los Angeles AQCR. This represents a substantial reduction from the 1970 emission level (as reported by the LA APCD and the ARB) due to the introduction of modified combustion control on JT8D engines. The 1972 ARB/APCD estimate will be used in the present study.

Piston Aircraft

The 1972 ARB/APCD inventory indicates 22 tons per day of organic emissions from piston aircraft in the Los Angeles AQCR. This value will be used in the present study.

2.1 REFERENCES

1. H. Linnard, Personal Communication of Data in the Preliminary 1972 Emission Inventory, California Air Resources Board, Sacramento, California, January 1975.

2. EPA Office of Air Quality Planning and Standards, 1972 National Emissions Report, "National Emission Data System (NEDS) of the Aerometric and Emission Reporting System (AEROS)", EPA-450/2-74-012, June 1974.

3. S. Weiss and G. Thomas, Personal Communication of Data in the 1972 Los Angeles County APCD Emission Inventory, January 1975.

4. T. Peng, Personal Communication of Emission Inventory Data, "Automotive Power Systems Evaluation Study", Jet Propulsion Laboratory, Pasadena, California, January 1975

5. J. Trijonis, G. Richard, K. Crawford, R. Tan, and R. Wada, An Implementation Plan for Suspended Particulate Matter in the Los Angeles Region, (Technical Support Document #2, Emission Inventories and Projections), EPA Contract #68-02-1384, TRW Environmental Services, March 1975.

6. R. Murray, Personal Communication, Los Angeles County Air Pollution Control District, February 1975.

7. G. Thomas, Personal Communication, Los Angeles County Air Pollution Control District, February 1975.

8 M. F. Brunelle, J. E. Dickinson, and W. J. Hamming, Effectiveness of Organic Solvents in Photochemical Smog Formation, Solvent Project - Final Report, Los Angeles County Air Pollution Control District, July 1966.

9. Environmental Protection Agency, "Compilation of Air Pollutant Emission Factors", AP-42, 2nd Edition, April 1973.

10. F. P. Grad et al, "The Automobile and the Regulation of its Impact on the Environment", Columbia University, New York, February 1974.

11. CALSPAN Corporation, "Automobile Exhaust Emission Surveillance, A Summary", EPA Contract No. 68-01-0435, Publication No. APTD-1544, May 1973.

3.0 COMPOSITION DATA FOR ORGANIC EMISSION SOURCES

The overall contribution of an organic source type to oxidant formation is a product of two factors, the total amount of organics emitted and the reactivity of those organics. In order to determine the reactivity of organic emissions from sources in the Metropolitan Los Angeles Air Quality Control Region (AQCR), it was necessarv to accumulate data on the composition of those emissions. Specifically, for this study a composition breakdown was required for each source according to the five class reactivity categorization. The purpose of this chapter is to present and discuss the available organic emission composition data, to describe how the data were evaluated and incorporated into the various reactivity schemes, and to explain the necessity and rationale for making certain assumptions in the composition and molecular weight estimates.

Due to variations in the type of industries in a given area, differences in local air pollution regulations, and other factors, the composition of emitted organics varies from one location to another. The data accumulated for this study are intended as an average for the Metropolitan Los Angeles Air Quality Control Region and are strictly applicable only to this region.

In order to derive emission reductions (Chapter 5) and evaluate alternative control strategies (Chapter 6), it was necessary that emission composition data be assembled for all source types in the emission inventory (Chapter 2). For a few of these sources, detailed and representative composition data were readily available. However, for many sources, the best available data were incomplete and lacking in detail. For this reason, it was necessary, in many cases, to use the incomplete data and reasonable assumptions in order to arrive at detailed composition estimates.

Section 3.1 describes how the various data sources were used, how conflicts in data from various sources were resolved, and how the reliability of each data source was evaluated. It also describes the procedures used to make the necessary approximations and extrapolations in the cases where sufficiently detailed data were not available. Section 3.2 presents the hydrocarbon composition data for emissions from stationary sources involving organic fuels and combustion. These sources include petroleum production, refining, gasoline marketing, fuel combustion, and waste burning & fires. Section 3.3 presents composition data for chemical process emissions and solvent evaporation. The sources in this category include surface coating, dry cleaning, degreasing, printing, and other chemical operations. Section 3.4 deals with the composition of emissions from mobile sources including light and heavy duty gasoline powered vehicles, diesel powered vehicles, and aircraft. Finally, Section 3.5 summarizes and discusses the composition data.

3.1 DATA POLICIES AND ASSUMPTIONS

Since data on hydrocarbon composition for every source type in the Metropolitan Los Angeles AQCR are not available, the estimates derived in this chapter involve many approximations. This section discusses the types of approximations that were made and the basis for making them.

3.1.1 Sources of Composition Data

For many of the emission categories listed in the inventory, there was only one source of information regarding the composition of the organic emissions. When this was the case, the composition breakdown was based on this single data source. In many cases, however, there were several sources of data. When this occurred, the most appropriate source was selected based on the following criteria:

- Comprehensiveness. For some source categories, a comprehensive list of all the organic emissions and the mole % of each type of compound was available. This type of information was the most useful since it was possible to insert each individual compound into the reactivity scheme without making arbitrary assumptions.

- Representativeness. Since data obtained from a small number of sources was extrapolated to all sources in a given category, care had to be used to assure that the data was representative of the sources in that category. If the tested sources were unusual or non-typical, the results could not be considered to be representative of the whole class.

- Age of the data. If two sources of data were available, the most recent was given higher priority since, presumably, the accuracy of the analysis would have improved due to advances in the techniques of analytical chemistry.

- Consistency. Each data source was critically compared to the other data sources for that category, and an evaluation was made regarding the quality of the data source. This procedure was used in order to detect any data that were clearly in error. This does not mean that all sources agreed completely, but that any large disagreements were considered cause for a more detail evaluation of the reliability of the data.

3.1.2 Composition Estimates

Although the methods used to determine the final organic composition for a given source varied from one category to the next depending on the type of data that were available, in general the composition was arrived at by similar means for all sources. The first step was to determine which test data were the most reliable by considering the factors outlined earlier. If these were detailed enough, the various compounds or compound types were assigned to a category in the five class reactivity categorization. If the data were less detailed than necessary, assumptions were made to attain the required detail. When it was necessary to make assumptions of composition, the following bases were used:

- Knowledge of the prosesses involved - for example, emissions from plastics manufacturing facilities would be expected to be rich in low molecular weight olefins (ethylene, propylene, butylene and isobutylene) and styrenes (styrene and α-methyl styrene).
- Similarity to other emission sources - where applicable, the composition of the emissions from one source were estimated by considering the known emissions from a similar source.
- Estimation based on what does not seem unreasonable - where there was no other basis, estimates were developed based on general familiarity with organic mixtures and were checked to see if the results were reasonable.

In the sections that describe the composition of each source category (Sections 3.2.1 through 3.4.5), an indication of the method used in arriving at the hydrocarbon breakdown is presented. In those cases where an arbitrary assumption was made, the data should be used only with caution and the inherent uncertainty should be noted.

Fortunately, the sources that emit the largest amounts (tons/day) of hydrocarbons tend to be those for which the most detailed data are available. The effect of this is that detailed composition data were obtained for a large portion of the total organic emissions. Most of the uncertainty in the composition data occurs in the sources that have small emission rates. Therefore, although a large uncertainty in the composition, and ultimately the reactivity index, can occur in some of the small emission sources, the uncertainty in the overall inventory is relatively small.

3.1.3 Estimation of Average Molecular Weights

The average molecular weight of the compounds in a given category was determined by using:

- The known molecular weight for categories that consist of a single compound;
- A weighted average of the compounds in a given category when detailed composition data were available;
- Estimated molecular weights where no other data were available (frequently it was necessary to estimate a molecular weight in order to determine the composition).

The average molecular weight of the emissions from each source was calculated from the average molecular weight of each composition category and the mole fraction of each category. Detailed information regarding the calculation of average molecular weights for each source type is presented in Appendix A.

3.2 STATIONARY SOURCES - ORGANIC FUELS AND COMBUSTION

The sources included in this category are those related to organic fuels and combustion in stationary sources. The organics emitted by sources in this category are of 3 main types: evaporated fuel, incompletely combusted fuel and pyrolysis products. The major source types included in this category are:

- Petroleum Production and Refining
- Gasoline Marketing
- Fuel Combustion
- Waste Burning and Other Fires

3.2.1 Petroleum Production and Refining

Petroleum Production

The organics that are emitted by petroleum producing operations are primarily the result of treating the petroleum at the drilling site (petroleum production refers to removing oil and gas from the ground, not oil refining). Typically, oil that is pumped directly out of the ground is mixed with salt water and gaseous hydrocarbons such as methane, ethane, etc. Usual practice is for the water and the light gases to be separated at the drilling site, and in many cases, for the water to be reinjected into the well. The light gases are then compressed causing some of the heavier components and water vapor to condense. After these components are separated, the light gases are transported by pipeline to other processing facilities or to be used as fuel without further treatment [1].

The organics are emitted in petroleum production from storage tanks, run down tanks, oil/water separators and vents. These facilities are subject to disruptions and breakdowns, during which the light hydrocarbon gases are released directly into the atmosphere. Also, during the initial start up of a new well, before the treating facilities have become operational, large volumes of light hydrocarbons are vented to the atmosphere [1].

Table 3-1 shows an estimate, based on a 1957 study, of the composition of the organics emitted by these processes. Since the composition would be expected to vary from one field to another, the data in Table 3-1 represent an average for three Los Angeles area oil fields [1].

Table 3-2 presents the hydrocarbon breakdown for petroleum production according to the 5 reactivity categories.

Petroleum Refining

Although the refining of crude oil is a very complicated process, all refining operations can be broken down in a few basic processes.

The primary refinery process is distillation. Distillation is a separation process whereby the very complicated mixture of chemical compounds which make up crude oil is separated by boiling point into a number of fractions. Each fraction consists of a smaller number of chemical compounds, all of whose boiling points fall into a relatively small range.

TABLE 3-1 ESTIMATED COMPOSITION OF THE ORGANIC EMISSIONS DUE TO PETROLEUM PRODUCTION [1]

Mole % *

Methane	63.9	Hexane	1.0
Ethane	11.3	Cyclohexane	1.7
Propane	8.5	Heptane	1.2
n-Butane	4.9	Cycloheptane	0.3
i-Butane	2.1	Cyclooctane	0.2
n-Pentane	1.7	Nonane	0.2
i-Pentane	1.5	Benzene	0.1
Cyclopentane	0.4	Toluene	0.1

*It was assumed the volume % equals mole %.

Distillations are routinely carried out at reduced, ambient, and elevated pressures. Since the boiling point changes with pressure, selection of the appropriate pressure allows gaseous compounds such as methane, ethane, propane, ethlyene, etc. to be separated by high pressure distillation. At the other extreme, low pressure, or vacuum distillation, allows separation of higher boiling fractions without the use of excessive temperatures which would lead to coking problems.

After the crude oil is separated into fractions, specific fractions are reblended to provide fuels that meet volatility, density, specific gravity, octane and other specifications.

Since crude oils do not in general contain the mixture of chemical compounds that corresponds to the commercially desirable mixture, large amounts of crude oil are converted into more saleable products. Among these conversion processes are cracking, reforming, and alkylation. The operating principles vary considerably from one process to the next, but in all cases, the basic principle is that a process stream is treated in such a manner

TABLE 3-2 ESTIMATED COMPOSTION OF ORGANICS EMITTED BY PETROLEUM PRODUCING OPERATIONS [1]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	84	Mono-tert-alkyl benzenes		C_{4+}-paraffins	13	Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins	3	Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	84	TOTAL CLASS II	0	TOTAL CLASS III	16	TOTAL CLASS IV	0	TOTAL CLASS V	0

that undesirable chemical compounds are converted to desirable ones. For example, catalytic cracking typically consists of converting gas oil (medium hydrocarbons) to lighter hydrocarbons, many of which are gasoline components.

In addition to these primary operations, there are various miscellaneous processes such as desalting, sulfur removal, vis-breaking, etc., which are employed to remove impurities or modify the physical properties of the crude oil or products.

Due to the large number of refinery emission sources, and the large number of separations, conversions and recombinations involved, it would be very difficult to estimate the composition of the emissions based on the crude oil feeds and the product output. Furthermore, even if the composition of all streams could be estimated, it would be very difficult to estimate what weighting factor to apply to each stream to allow a reasonably correct estimate of overall emissions, [2].

The most appropriate method of determining refinery hydrocarbon emissions is to measure the emission rate and the composition of the emissions from a statistically significant number of sources and from this extrapolate to the total emissions, [2]. A study of this sort was done for refineries in Los Angeles County [3], and although it lacks detailed composition data, it is regarded as the best available data, [2], [4], [5], [6], [7], [8]. The estimates described below were made based on this information.

Table 3-3 shows the breakdown of emissions from several refinery sources by three classes of compounds: olefins, aromatics except benzene, and other hydrocarbons including benzene. The data in this table represent the time period July 1971 to June 1972. Data from another source was used to estimate emissions from crude and distillate storage (Note that the emissions due to surface coating are reported in Section 3.3.1.) These sources were combined to give an estimate of the total organic emissions as shown in Table 3-4.

TABLE 3-3 SUMMARY OF ORGANIC EMISSIONS FROM REFINERY SOURCES

Emission Source [2]	Olefins	Aromatics, Except Benzene	Other Hydrocarbons Including Benzene	Total
Catalytic Cracking	0	0	0.05	0.05
Separators and Sewers	0.31	0.21	1.17	1.69
Pressure Relief Values	0.20	0.20	1.28	1.68
Blowdowns and Turnarounds	0.01	0	1.15	1.16
Vessel and Tank Maintenance	0	0	0.42	0.42
Cooling Towers	0.31	0.21	1.54	2.06
Pump Seals (Packing Glands)	0.71	0.62	4.54	5.87
Valves and Flanges	1.39	1.02	6.78	9.19
Compressor Exhaust	0.02	0	2.70	2.72
Compressor Seals	0.32	0.10	1.35	1.77
Heater Stacks *	0.01*	0	0.41*	0.42*
Other +	0.11	0.16	1.44	1.70
	3.38 (tons/day)	2.52 (tons/day)	22.42 (tons/day)	28.32 (tons/day)
Fuel Combustion* [9]				4.4*
Storage [9]				
Distillates				12.3
Crude				8.8
				49.4 tons/day*

* Fuel combustion is considered in Section 3.2.3; emissions from this source are shown for reference but are not included in the totals; (0.42 tons/day applies only to heaters; Ref. [9] shows 4.8 tons/day for all combustion devices; 4.8 - 0.42 = 4.4 tons/day for combustion devices other than heaters.)

+ Losses from blind changes, sampling, treating, vacuum jets, barometric condensors, air blowing, etc.

TABLE 3-4. ORGANIC EMISSIONS FROM EACH TYPE OF REFINERY SOURCE [3], [9]

Type of Source

Emission Source	Tons/Day	% of Total Hydrocarbon Emissions
Storage (SH)		
Distillate	12.3	24.9
Crude Oil	8.8	17.8
	21.1	42.7
Pumping (SH)		
Valves and Flanges	9.19	18.6
Packing Glands (Pump Seals)	5.87	11.9
Pressure Relief Valves	1.68	3.4
	16.74	33.9
Compressors (SH)		
Drive Engine Exhaust	2.72	5.5
Seals	1.77	3.6
	4.49	9.1
Other Operations (OS) (Vacuum Jets, Barometric Condensers, Blind Changing, etc.)	1.7	3.4
	1.7	3.4
Cooling Towers (SC)	2.06	4.2
	2.06	4.2
Separators and Sewers (OS)	1.69	3.4
	1.69	3.4
Blowdowns and Turnarounds (OS)	1.16	2.3
	1.16	2.3
Vessel and Tank Maintenance (OS)	0.42	0.9
	0.42	0.9
Catalytic Cracking (SC)	0.05	0.1
	0.05	0.1
	49.4	100%

(SH)	Storage and Handling
(SC)	Separation and Conversion Processes
(OS)	Other Sources

4.8 Tons/Day of organics are emitted from combustion sources, [3], [9], and 1.5 tons/day are due to evaporation from surface coatings, [8], [9];

NOTE: The value of 10 tons/day for surface coating evaporation, Ref. 9, page 24, is in error - the correct value is shown, [8].

The major source of refinery emissions is related to storage and handling of crude oil and distillate products. Table 3-4 shows that approximately 85.7% of the total refinery hydrocarbon emissions are due to storage, pumping and compression. About half of these emissions (42.7% of the total) are due to storage of crude oil and distillates. These emissions are due primarily to leaks at the seals of floating roof tanks, breathing, and vapor displacement in fixed roof tanks, and boiling in both types of tanks.

The emissions from separation and conversion processes are related primarily to combustion and cooling tower losses. Organic emissions from combustion processes are the result of incomplete combustion of fuels, whereas the emissions from cooling towers are a result of oil leaking into the water which is used for evaporative cooling, [10]. Some hydrocarbons are emitted directly from catalytic cracking units. Table 3-4 shows the fraction of emissions from these sources to be about 4.3% of the total refinery organic emissions.

The remainder of the organic emissions, about 10.0%, are comprised of emissions from a variety of other sources as listed in Table 3-4.

Although there are some data available regarding the composition of refinery emissions, the detailed information necessary for a study of this sort is not. Therefore, any estimated composition of these emissions is necessarily based on very limited information and on approximations whose uncertainty is quite large. The information in Table 3-5, then, is only a rough approximation of the composition of refinery emissions.

Table 3-6 shows the estimated breakdown of refinery hydrocarbon emissions based on the 5-class reactivity categorization.

3.2.2 Gasoline Marketing

Underground Gasoline Storage Tanks

There are two primary mechanisms by which underground gasoline storage tanks emit organics. The first of these is commonly known as "breathing", [10]. As the hydrocarbon vapors which have accumulated over liquid gasoline are warmed by an increase in ambient temperature, they expand and are forced out through the tank vent.

TABLE 3-5 ESTIMATE OF THE COMPOSITION OF ORGANIC REFINERY EMISSIONS

Type or Source of Emission	Estimated Mole % Of Type Of Source	Estimated Mole % Of Total	Comments
Olefins[3]	100%	6.9	Straight forward; from Table 3-3.
Aromatics, Except Benzene[3]	8% Mono-Tertiary Benzenes	0.2	Estimate; any errors are likely to have a small effect since these organics account for a small fraction of the total.
	15% Primary and Secondary Alkyl Benzenes	0.8	
	70% Dialkyl Benzenes	3.8	
	7% Tri- and Tetra-Alkyl Benzenes	0.3	
		5.1	
Other Hydrocarbons, Including Benzene[3]	3% Acetylene	1.4	Estimate based on whole gasoline composition data*; any errors are likely to have a large effect since these organics account for a large fraction of the total.
	1% C_1 - C_3 Paraffins	0.9	
	5% Benzene	2.3	
	44% C_{4+} Paraffins	41.6	
		46.2	
Distillate Storage[9]	59% C_{4+} Paraffins	14.7	Estimate based on underground gasoline storage tank vapors. Any errors are likely to have a large effect since these organics account for a large fraction of the total.
	22% Olefins	5.5	
	19% C_1 - C_3 Paraffins	4.7	
		24.9	
Crude Storage[9]	61% C_{4+} Paraffins	10.8	Estimate based on whole gasoline; any errors are likely to have a substantial effect since these hydrocarbons account for a significant fraction of the total.
	13% Primary and Secondary Alkyl Benzenes	2.3	
	10% Olefins	1.8	
	11% Dialkyl Benzenes	2.0	
	1% Cycloparaffins	0.1	
	1% Tri- and Tetra-Alkyl Benzenes	0.2	
	1% Benzene	0.2	
	2% Acetylene	0.4	
		17.8	

---

*There are very small quantities of or no cycloparaffins, aldehydes, ketones, or alcohols in crude oil or petroleum products. [11], [12], [13], [14].

TABLE 3-6 ESTIMATED COMPOSITION OF THE ORGANICS EMITTED FROM REFINERY OPERATIONS [2], [3], [8], [9]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	6	Mono-tert-alkyl benzenes		C_{4+}-paraffins	67	Prim-& sec-alkyl benzenes	3	Aliphatic olefins	14
Acetylene	2	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	5	α-methyl styrene	
Benzene	3	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	11	TOTAL CLASS II	0	TOTAL CLASS III	67	TOTAL CLASS IV	8	TOTAL CLASS V	14

The second mechanism operates while the storage tanks are being filled by tanker truck. As gasoline is dumped into the tank, the liquid displaces an equal volume of vapor which is then vented to the atmosphere. The composition of these vapors is similar to those emitted by the first mechanism with some variations possible due to temperature differences.

Since the vapors accumulate over the gasoline during a relatively long period of time, the composition of the vapors should approach the equilibrium composition. Table 3-7A shows equilibrium composition data for a regular grade and premium grade of gasoline at 79°-80°F. This is compared to composition data for two fuels measured at the vent of actual gasoline storage tanks. As shown in Table 3-7B, the main difference between the two compositons is in the amount of Class I compounds. The composition measured at the tank vents was used to estimate the reactivity of these emissions.

In order to compensate for the differences in the composition of the hydrocarbons emitted from these tanks, the composition breakdown presented in Table 3-8 is weighted to account for the relative amounts of regular grade and premium grade gasoline that were sold in 1972. For that time period the ratio was 30% regular and 70% premium on a volume basis, [15], [16]. After 1972 the ratio changed radically in the direction of an increasing fraction of regular grade until (in early 1975) the ratio was approximately 55% regular and 45% premium, [15]. Furthermore, as increasing numbers of automobiles which are equipped to run on unleaded regular are produced, the fraction of regular gasoline will continue to increase, [15].

Automobile Gasoline Tank Filling

During the filling of automobile gasoline tanks, hydrocarbons are emitted by two primary mechanisms: gasoline vapor displacement and liquid gasoline spillage. The composition of the hydrocarbons emitted by each mechanism is different since the first is essentially the equilibrium vapors that collect above liquid gasoline and the second is whole gasoline. The weight of hydrocarbons emitted by each of these processes is about 12.5 lbs/1000 gal. transferred due to vapor displacement and 3.0 lbs/1000 gal. transferred due to spills, [17]. This is equivalent to 81% by vapor displacement and 19% due to spills.

TABLE 3-7A EQUILIBRIUM COMPOSITION OF GASOLINE VAPORS OVER LIQUID GASOLINE [14]

Class	Regular Grade (80°F), Mole %	Premium Grade (79°F), Mole %
Class I	5	3
Class II	0	0
Class III	66	78
Class IV	3	4
Class V	26	15
	100%	100%

TABLE 3-7B COMPOSITION OF THE EMISSIONS FROM UNDERGROUND GASOLINE STORAGE TANKS [14]*

Class	Regular Grade, Mole %	Premium Grade, Mole %
Class I	20	17
Class II	0	0
Class III	57	61
Class IV	0	0
Class V	23	22
	100%	100%

* For complete composition data see Table B-1.

TABLE 3-8 COMPOSITION OF ORGANICS EMITTED FROM UNDERGROUND GASOLINE STORAGE TANKS* [14]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	18	Mono-tert-alkyl benzenes		C_{4+}-paraffins	59	Prim-& sec-alkyl benzenes		Aliphatic olefins	22
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	18	TOTAL CLASS II	0	TOTAL CLASS III	60	TOTAL CLASS IV	0	TOTAL CLASS V	22

*Weighted average of regular grade and premium grade storage tanks based on 1972 gasoline sales of 30 volume % regular grade and 70 volume % premium grade.

Data is available which shows the composition of the equilibrium vapors above both liquid regular and premium grade gasolines at two temperatures (79-80°F and 85°F), [3]. Since the yearly average ambient temperature is about 60°F ,[18], [19], and since it is usually assumed that the operating temperature of automobile fuel tanks is about 10°F higher than ambient, (due to sloshing, heat from the hot parts of the automobile, etc., [16]) the composition of the equilibrium vapors at 79-80°F is most representative of the vapors displaced during automobile tank filling.

Table 3-9 shows the classes of compounds in both regular and premium grade gasoline vapors at two temperatures. Table 3-10 shows the classes of compounds in a regular and premium grade Los Angeles area gasoline. It should be noted that the composition of gasoline is quite variable. The composition is adjusted to have the appropriate characteristics for the region in which it will be sold and for the time of year that it will be sold. For example, gasoline blended for use at high temperatures and high altitudes has fewer low boiling components than one blended for use in a cold climate at sea level.

The composition of the hydrocarbons emitted due to automobile tank filling, as shown in Table 3-11, is a weighted average of gasoline vapors and whole gasoline, which takes into account the ratio of vapor to whole gasoline losses (81% and 19% respectively) and the relative amounts of regular and premium grade consumed (30% and 70% respectively).

3.2.3 Fuel Combustion

In theoretically perfect combustion all of the organic fuel is converted to carbon dioxide and water. In actual practice, however, incomplete combustion occurs, with the result that organic compounds are emitted from most combustion devices. These emissions are the result of at least three separate processes. First, some raw fuel is emitted from leaks and spills, second, unburned or partially burned fuel is emitted from the stack,

TABLE 3-9 EQUILIBRIUM VAPORS ABOVE LIQUID GASOLINE [3]

Class	Regular Grade Gasoline, Mole % 80°F	Regular Grade Gasoline, Mole % 85°F	Premium Grade Gasoline, Mole % 79°F	Premium Grade Gasoline, Mole % 85°F
Class I	5	5	3	2
Class II	0	0	0	0
Class III	66	67	78	80
Class IV	3	2	4	3
Class V	26	26	15	15
	100%	100%	100%	100%

For additional composition data see Tables B-2 through B-7.

TABLE 3-10 HYDROCARBON COMPOSITION OF LOS ANGELES AREA GASOLINES [3]

Class	Regular Grade Gasoline, Mole %	Premium Grade Gasoline, Mole %
Class I	7	4
Class II	0	0
Class III	54	48
Class IV	20	34
Class V	19	14
	100%	100%

For additional composition data see Tables B-8 through B-11.

TABLE 3-11 COMPOSITION OF ORGANICS EMITTED DUE TO AUTOMOBILE GASOLINE TANK FILLING* [3], [15], [16], [17]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	2	Mono-tert-alkyl benzenes		C_{4+}-paraffins	60	Prim-& sec-alkyl benzenes	5	Aliphatic olefins	17
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	4	α-methyl styrene	
Benzene	2	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	1
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	4	TOTAL CLASS II	0	TOTAL CLASS III	60	TOTAL CLASS IV	9	TOTAL CLASS V	18

*Assuming 30 volume % regular and 70 volume % premium grade consumed, and 81 weight % emitted by vapor displacement and 19 weight % emitted due to spillage.

finally, decomposition products from the fuel (or "cracking products") are formed when the fuel is subjected to high temperatures in or near the combustion zone.

As might be expected, this results in a complex mixture of products. Table 3-12 shows the estimated composition of the hydrocarbon emissions due to fuel combustion. Since these are working estimates only, and not actual test results, they are subject to a high degree of uncertainty and should be used with caution.

The composition data, broken down into the 5-class reactivity scheme, is shown in Table 3-13.

TABLE 3-12. ESTIMATED COMPOSITION OF THE ORGANICS EMITTED DURING FUEL COMBUSTION

COMPOUND OR COMPOUND TYPE	ESTIMATED WEIGHT %	ACTUAL OR ESTIMATED MOLECULAR WEIGHT	MOLE %
Methane	50	16 (-)	78
Ethane	5	30 (-)	4
Propane	5	44 (-)	3
Acetylene	5	26 (-)	5
C_{4+} Paraffins	10	86 (C_6)	3
Primary and Secondary Alkylbenzenes	5	120 (C_9)	1
Aliphatic	10	70 (C_5)	3
Aliphatic Aldehydes	10	66 (C_5)	3
	100%		100%

TABLE 3-13 COMPOSIITON OF THE ORGANICS EMITTED DURING FUEL COMBUSTION

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	85	Mono-tert-alkyl benzenes		C_{4+}-paraffins	3	Prim-& sec-alkyl benzenes	1	Aliphatic olefins	3
Acetylene	5	Cyclic ketones		Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	3
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	90	TOTAL CLASS II	0	TOTAL CLASS III	3	TOTAL CLASS IV	1	TOTAL CLASS V	6

3.2.4 Waste Burning and Other Fires

The organic emissions from waste burning and other fires results primarily from incomplete combustion and decomposition of various materials. An estimate of the composition of the hydrocarbons emitted by these sources is shown in Table 3-14, [20].

Table 3-15 shows these data in the 5-class reactivity scheme.

TABLE 3-14. ESTIMATED COMPOSITION OF THE ORGANICS EMITTED DUE TO WASTE BURNING AND OTHER FIRES

COMPOUND TYPE	WEIGHT % [20]		ACTUAL OR ESTIMATED MOLECULAR WEIGHT	MOLE %
Methane	34		16 (-)	59
Other Paraffins	12			
C_2-C_3		(4*)	37 ($C_{2.5}$)	3
C_4+		(8*)	86 (C_6)	3
Ethylene	12		28 (-)	12
Other Olefins	2		70 (C_5)	1
Carbonyls	14			
Ketones		(4*)	72 (C_4)	2
Aldehydes		(10*)	86 (C_5)	3
Other Oxygenates	10			
Primary and Secondary			74 (C_4)	2
Alkyl Alcohols		(6*)	32 (-)	4
Methanol		(4*)		
Aromatics	4			
Dialkyl Benzenes		(3*)	120 (C_9)	1
Tri - and Tetra-Alkyl Benzenes		(1*)	162 (C_{12})	0
Acetylene	12			
Acetylene		(8*)	26 (-)	8
C_3+ Acetylenes		(4*)	54 (C_4)	2
	100%			100%

*Estimated

TABLE 3-15 COMPOSITION OF THE ORGANICS EMITTED BY WASTE BURNING AND OTHER FIRES [20]

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	62	Mono-tert-alkyl benzenes		C_{4+}-paraffins	3	Prim-& sec-alkyl benzenes		Aliphatic olefins	13
Acetylene	8	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	1	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes	2	Branched alkyl ketones		Aliphatic aldehydes	3
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols	2	Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones	2	Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol	4								
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	74	TOTAL CLASS II	0	TOTAL CLASS III	7	TOTAL CLASS IV	3	TOTAL CLASS V	16

3.3 STATIONARY SOURCES - ORGANIC CHEMICALS

The sources indicated in this category are those due to chemical manufacturing and solvent evaporation.

The major source types included in this category are:

- Surface coating solvent evaporation
- Dry cleaning
- Degreasing
- Printing
- Industrial Processes

3.3.1 Surface Coatings

Heat Treated Coatings

The hydrocarbons that are released during the heat treating of some types of coatings are highly localized and therefore are subject to emission controls. Since the usual control mechanism is an afterburner, it would be expected that the ultimate emissions would differ in character from the emissions from air cured coatings.

Table 3-16 shows the approximate composition of such emissions as determined by measurements of a number of heat treating facilities, along with the average measured concentration. Table 3-17 shows the same information in the 5-class reactivity scheme format.

Air Dried Coatings

Significant amounts of organics are released during the curing of surface coatings (paint). These organic solvents are used to give the coatings the appropriate properties for spreading, covering, etc. and then are allowed to evaporate as the coating cures.

The composition of these solvents used in the Los Angeles are regulated by Los Angeles County Air Pollution Control District Rule 66 and

TABLE 3-16. AVERAGE DISTRIBUTION OF THE ORGANIC COMPOUNDS EMITTED DURING HEAT TREATING OF COATINGS [21]

Compound Type	Mole %	ppm*
C_{1-3} Paraffins	20	25.5
C_4+ Paraffins	28	36.2+ †
	0	0.3
Olefins	2	2.4
Acetylene	0	0.3
Primary and Secondary Alkyl Benzenes	35	45.6+
Dialkyl Benzenes	15	20.0+

* Expressed as ppm value of compound; original references expressed in ppm carbon.

+ A total of 770 ppm carbon, convered to 85.6 ppm by assuming average of C_9 compounds.

+ 16.2 ppm measured; additional 20 ppm estimated.

TABLE 3-17 APPROXIMATE COMPOSITION OF THE ORGANICS EMITTED DURING HEAT TREATING OF SURFACE COATINGS [21]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	20	Mono-tert-alkyl benzenes		C_{4+}-paraffins	28	Prim-& sec-alkyl benzenes	35	Aliphatic olefins	2
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes	15	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	20	TOTAL CLASS II	0	TOTAL CLASS III	28	TOTAL CLASS IV	50	TOTAL CLASS V	2

comparable rules in the adjoining counties. These rules limit the use of photochemically reactive solvents. LAC APCD Rule 66 (k) [22] reads, part:

Rule 66

> k. For the purposes of this rule, a photochemically reactive solvent is any solvent with an aggregate of more than 20 per cent of its total volume composed of the chemical compounds classified below or which exceeds any of the following individual percentage composition limitations, referred to the total volume of solvent:
>
> 1. A combination of hydrocarbons, alcohols, aldehydes, esters, ethers or ketones having an olefinic or cyclo-olefinic type of unsaturation: 5 per cent;
> 2. A combination of aromatic compounds with eight or more carbon atoms to the molecule except ethylbenzene: 8 per cent;
> 3. A combination of ethylbenzene, ketones having branched hydrocarbon structures, trichloroethylene or toluene: 20 per cent.

Since neither the LA APCD, the paint distributors, nor the manufacturers keep records of the composition of the surface coating solvent mixtures, the only information available is the national average solvent composition, [23], [24], [25]. As can be seen in Table 3-18 this average violates Rule 66. The paint manufacturers indicated that Rule 66 is met by substituting aliphatic and oxygenated hydrocarbons for the regulated ones in a two to one ratio, that is, two parts aliphatics to one part oxygenates,[25] (mole fraction assumed). Table 3-18 shows the effect of replacing a total of about 13.4% of the regulated compounds with aliphatics and oxygenates in the correct ratio.

Table 3-19 shows the distribution of the organics emitted by surface coatings according to the 5-class reactivity scheme.

Using LA APCD Rule 66, and assigning a value of one to reactive hydrocarbons and zero to unreactive, a molar reactivity rating of 0.18 was calculated for emissions from this source using the LA APCD reactive-unreactive reactivity scheme. Similarly, the reactivity calculated for the emissions from heat treated coatings is 0.52. This agrees with the fact that the LA APCD considers the emissions from heat treating operations to be more reactive than the emissions from air dried coatings, [23].

TABLE 3-18 COMPOSITION OF SURFACE COATING SOLVENTS [22], [25]

	ACTUAL OR ESTIMATED MOLECULAR WEIGHT	1972 ANNUAL NATION-WIDE CONSUMPTION, lbs. PER CAPITA	COMPOSITION OF SOLVENTS [illegible], MOLE %† OF TOTAL HYDROCARBONS	REDUCTION REQUIRED BY LAC APCD - RULE 66	SUBSTITUTION OF OTHER COMPOUNDS	ESTIMATED COMPOSITION OF [illegible] IN THE LOS ANGELES AREA, MOLE %† OF TOTAL HYDROCARBONS
ALIPHATIC HYDROCARBONS						
Mineral spirits, regular, low odor	86* (C_6)	2.085	16.9		Unknown mixture of C_6* paraffins	Unknown mixture of C_6* paraffins
Mineral spirits, odorless	86* (C_6)	0.386	2.9			
Kerosene	142 (C_{10})	0.053	0.3			
Mineral spirits, heavy, coal-oil	86* (C_6)	0.166	1.7			
Other aliphatic hydrocarbons	86 (C_6)	[illegible]	0.1			
		[illegible]	27.8		8.9	30.7
AROMATIC & NAPHTHENIC HYDROCARBONS						
Benzene	78 (-)	0.033	0.3			0.3
*Toluene (Rule 66-K-1)	92 (-)	1.667	12.1	3.0		8.7
*Xylene (Rule 66-K-2)	106 (-)	2.277	13.8	7.0		6.8
Naphtha, high flash	130* (C_{10})	0.462	2.1			2.1
*Other aromatics (Rule 66-K-2)	120* (C_9)	0.986	7.6	1.5		1.1
Naphthenic hydrocarbons	140* (C_{10})		2.2			2.2
		[illegible]	[illegible]	12.7		[illegible]
TERPENIC HYDROCARBONS						
(Pine oil & turpentine)	136* (C_{10})	[illegible]	0.1			0.1
ALCOHOLS (MONOHYDRIC)						
Methyl Alcohol ("methanol")	32 (-)	0.004	1.0		2.0	3.0
Ethyl alcohol (inc. all denatured grades)	46 (-)	0.077	1.0			1.0
Propyl alcohol (n. & iso.)	60 (-)	0.204	2.0			2.0
N. butyl alcohol	74 (-)	0.370	3.3			3.3
Other butyl alcohols	74 (-)	0.033	0.3			0.3
Other monohydric alcohols	102* (C_6)	[illegible]	[illegible]			[illegible]
		[illegible]	[illegible]		2.0	[illegible]
GLYCOLS & DERIVATIVES						
Glycols	90* (C_6)	0.160	0.0			0.0
Glycol ethers (Cellosolves)	90* (C_6)	[illegible]	[illegible]			[illegible]
KETONES & ESTERS						
Acetone (di-methyl ketone)	58 (-)	0.002	7.1		2.5	9.6
Methyl ethyl ketone (M.E.K.)	72 (-)	0.080	0.2			0.2
*Methyl isobutyl ketone (Rule 66-K-3)	100 (-)	0.275	1.8	0.5		1.3
*Other ketones (Rule 66-K-3)	128* (C_8)	0.002	0.4	0.1		0.3
Ethyl acetate	88 (-)	0.029	0.2			0.2
Isopropyl acetate	102 (-)	0.020	0.2			0.2
Normal butyl acetate	116 (-)	0.311	1.7			1.7
Other esters	146* (C_8)	[illegible]	[illegible]			[illegible]
		7.262	[illegible]	0.6	2.5	[illegible]
CHLORINATED SOLVENTS						
Methylene chloride	86 (-)	0.043	0.4			0.4
*Tri-chloro ethylene (Rule 66-K-3)	130 (-)	0.030	0.2	0.1		0.1
Other chlorinated solvents	150* (C_6Cl_2)	[illegible]	[illegible]			[illegible]
		[illegible]	[illegible]	0.1		[illegible]
OTHER SOLVENTS & DILUENTS						
C_{10} + Cycloparaffins	140* (C_{10})	0.270	0.6			0.6
C_{10} + Paraffins	142* (C_{10})		0.6			[illegible]
		0.270	1.2			[illegible]
		[illegible]	[illegible]	13.[illegible]	13.[illegible]	[illegible]

* Estimated or assumed

* Use of these compounds limited by Los Angeles County Air Pollution Control District Rule 66-K

† Mole % assumed to equal volume %

TABLE 3-19 COMPOSITION OF THE ORGANICS EMITTED DURING CURING OF AIR DRIED SURFACE COATINGS [22], [25]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins	37	Prim-& sec-alkyl benzenes	9	Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins	5	Dialkyl benzenes	6	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones	2	Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols	12	Tri-& tetra-alkyl benzenes	1
Acetone	10			N-alkyl ketones	6	Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates	3	Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	4
Ethyl amines									
Dimethyl formamide									
Methanol	4								
Perhalogenated hydrocarbons									
Partially halogenated paraffins	1								
TOTAL CLASS I	15	TOTAL CLASS II	0	TOTAL CLASS III	51	TOTAL CLASS IV	29	TOTAL CLASS V	5

3.3.2 Dry Cleaning

As indicated in the emission inventory, there are basically two types of organic solvents used in dry cleaning operations in the Los Angeles Region. These are petroleum based solvent and "synthetic" solvent (perchloroethylene). The reactivity classifications for each type of solvent is treated individually below:

Dry Cleaners Using Petroleum Based Solvents

Table 3-20 presents composition data for several petroleum based dry cleaning solvents which are distributed in the Los Angeles area. With the exceptions of AMSCO 140-F which is particularly rich in napthenes and of SHELL SOL71 which has no aromatics, the solvents follow a consistent compositional pattern: about 1/3 paraffins, about 2/3 cycloparaffins, and a few percent aromatics. Solvents with atypical composition evidently are used for special purposes and do not account for much of the market, (AMSCO 140-F sales by one firm are reported as only 0.3% of AMSCO 20-H sales, [26]). For the purposes of this study, it will be assumed that the average composition of petroleum dry cleaning solvents in Los Angeles is 28% paraffins, 66% napthenes, and 6% aromatics. To obtain a more precise value for the average composition would require compositional and sales data for all solvents; these data were not available.

The paraffins in petroleum based dry cleaners solvent evidently are in the carbon number range C_{10} to C_{12}, [27]. Thus, they would all fall in Class III of the reactivity classification scheme, (as C_{4+} paraffins). The napthenes would also be in Class III, under the category cycloparaffins. The aromatics evidently are in the range C_8 to C_{12}, [27], [28]. One would expect that typical petroleum solvent C_8+ aromatics would be mostly Prim-& Sec-alkyl benzenes (Class IV) and Dialkyl benezenes (Class IV) with some Tri-& Tetra-alkyl benzenes (Class V). It is assumed that 5/6 of the C_8+ aromatics in petroleum dry cleaning solvent are in Class IV and 1/6 are in Class V. The sensitivity of the results to this assumption is low since the C_8+ aromatics constitute only a small fraction of petroleum dry cleaning solvent.

TABLE 3-20 COMPOSITION OF PETROLEUM DRY CLEANING SOLVENTS

COMPOUND TYPE	AMSCO			CHEVRON	SHELL	
	AMSCO 20-H (Stoddard) (a)	AMSCO 140-F (a)	AMSCO 365-H (Low End Point) (a)	CHEVRON 325 (El Segundo Output) (b)	SOL 360-EC (c)	SOL 71 (d)
Paraffins	25%	2%	25%	35.5%	91.7%	98%
Napthenes	67%	91%	68%	62.0%		
Aromatics	7%	7%	7%	2.5%	7.8%	0%
Olefins	---	---	---	---	0.5%	2%

DATA SOURCES:

(a) Ref. [28]
(b) Ref. [29]
(c) Ref. [30]

Table 3-21 summarizes the reactivity classification breakdown for petroleum dry cleaning solvents. It is evident that Class III predominates, although there are some contributions in Classes IV and V.

Dry Cleaners Using Synthetic Solvent (PCE)

The synthetic solvent used by dry cleaners is perchloroethylene, (PCE). PCE is a perhalogenated hydrocarbon and thus falls in Class I of the 5-class reactivity scheme. The classification for dry cleaners using synthetic solvent is thus as given in Table 3-22.

3.3.3 Degreasing

As indicated in the emission inventory, there are basically two types of organics used for degreasing operations in the Los Angeles Region. These are 1,1,1- Trichloroethane (1,1,1,-T) and Trichloroethylene (TCE). The reactivity classification for each of these compounds is given below:

TCE Degreasing

Trichloroethylene is a partially halogenated olefin and thus falls in Class IV of the reactivity classification scheme. Table 3-23 presents the reactivity categorization for this source.

1,1,1,-T Degreasing

1,1,1-Trichloroethane is a partially halogenated paraffin. Thus, it falls in Class I of the reactivity classification scheme. Table 3-24 presents the reactivity categorization for this source.

TABLE 3-21 REACTIVITY CLASSIFICATION FOR DRY CLEANERS USING PETROLEUM BASED SOLVENT [27], [28], [29], [30]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins	28	Prim-& sec-alkyl benzenes	5	Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins	66	Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	1
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	0	TOTAL CLASS II	0	TOTAL CLASS III	94	TOTAL CLASS IV	5	TOTAL CLASS V	1

TABLE 3-22 REACTIVITY CLASSIFICATION FOR DRY CLEANERS USING SYNTHETIC SOLVENT-PCE

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins		Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons	100								
Partially halogenated paraffins									
TOTAL CLASS I	100	TOTAL CLASS II	0	TOTAL CLASS III	0	TOTAL CLASS IV	0	TOTAL CLASS V	0

TABLE 3-23 ORGANICS EMITTED BY TCE DEGREASING OPERATIONS

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins		Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins	100	Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	0	TOTAL CLASS II	0	TOTAL CLASS III	0	TOTAL CLASS IV	100	TOTAL CLASS V	0

TABLE 3-24 ORGANICS EMITTED BY 1,1,1-T DEGREASING OPERATIONS

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins		Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins	100								
TOTAL CLASS I	100	TOTAL CLASS II	0	TOTAL CLASS III	0	TOTAL CLASS IV	0	TOTAL CLASS V	0

3.3.4 Printing

As indicated in the emission inventory (Chapter 2), organic emissions from the printing industry in the Los Angeles Region result from two types of printing: rotogravure and flexigraphic. The organic solvents typically used in rotogravure printing are substantially different from those used in flexigraphic printing. The reactivity classifiction scheme for each type of printing will be derived individually below:

Rotogravure Printing

Rotogravure printers use primarily two types of solvents. The large rotogravure plants which print advertisements and circulars use a solvent consisting of paraffins, naphthenes, and aromatics, [31]. The smaller rotogravure plants which perform printing for cartons and containers basically use an oxygenated, alcohol type solvent, [32]. Table 3-25 summarizes composition estimates for each type of rotogravure solvent, [32]. By combining these estimates with data on the relative usage of each solvent, the overall composition of rotogravure organic emissions can be calculated, (see right hand side of Table 3-25).

Table 3-27 shows the estimated composition of the organics emitted from this type of printing.

TABLE 3-25 ORGANIC COMPOSITION DATA FOR EMISSIONS FROM ROTOGRAVURE PRINTING [32]

	LARGE PLANTS	SMALL PLANTS	TOTAL
EMISSIONS AS % OF TOTAL	74%	26%	100%
Composition (by weight)			
Paraffins & Napthenes	83%	Negl.	61%
Aromatics	17%	Negl.	13%
Saturated Alcohols	Negl.	70%	18%
Saturated Acetates	Negl.	20%	5%
Other Esters	Negl.	10%	3%

TABLE 3-26 ESTIMATED COMPOSITION OF THE ORGANIC COMPOUNDS EMITTED BY ROTOGRAVURE PRINTING OPERATIONS [32]

COMPOUND TYPE	WEIGHT	ESTIMATED ON ACTUAL MOLECULAR WEIGHT	MOLE %
C_4+ Paraffins	51%	86 (C_6)	49.0
Napthenes (Cycloparaffins)	10%	112 (C_8)	7.3
Primary - and Secondary - Alkyl Benzenes	6%	106 (C_8)	4.7
Dialkyl Benzenes	7%	120 (C_9)	4.8
Methanol	6%	32 (-)	15.5
Other Saturated Alcohols	12%	74 (C_4)	13.4
Saturated Acetates	5%	116 (C_5)	3.6
Other Esters	3%	144 (C_7)	1.7
	100%		100%

Flexigraphic Printing

Flexigraphic printing uses an alcohol type organic solvent. Stationary source emissions specialists at the Los Angeles County APCD estimated that about 80% of the solvent (by weight) consists of alcohols and indicated that this was mostly isopropanol with some methanol, ethanol, and propanol, [31], [32]. The remainder of the solvent (approximately 20%) consists of ketones such as acetone and methyl ethyl ketone, [32]. Negligible amounts of paraffins, napthenes, and aromatics are emitted from flexigraphic printing.

Based on this information, Table 3-28 shows the estimated composition of organics emitted by flexigraphic printing.

TABLE 3-27 ESTIMATED COMPOSITION OF THE ORGANICS EMITTED BY ROTOGRAVURE PRINTING [32]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{6+}-paraffins	49	Prim-& sec-alkyl benzenes	5	Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins	7	Dialkyl benzenes	5	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols	13	Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates	5*	Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol	16								
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	16	TOTAL CLASS II	0	TOTAL CLASS III	61	TOTAL CLASS IV	23	TOTAL CLASS V	0

*Both saturated acetates and other esters are included in this category.

TABLE 3-28 ESTIMATED COMPOSITION OF THE ORGANIC COMPOUNDS EMITTED BY FLEXIGRAPHIC PRINTING OPERATIONS [32]

COMPOUND	WEIGHT %	MOLE %
Isopopanol	65	62.2
Methanol	5	9.0
Ethanol	5	6.3
n-Propanol	5	4.8
	80%	
Acetone	10	9.9
Methylethyl Ketone	10	8.0
	20%	100%

Table 3-29 shows these compounds categorized by the five class reactivity scheme.

3.3.5 Industrial Process Sources

Rubber, Plastic, Putty, and Adhesive Manufacturing

The present category includes the manufacture of rubber and plastic products as well as of putty and adhesives. The major sources in this category are rubber tire production and plastic manufacturing, [21].

Within the level of effort allocated to this study, it was not feasible to complete an up to date survey of organics emitted by these industries. Also, solvent manufacturers and distributors were unable to supply quantitative information on the sales of organics to these industries, [27], [34], [35]. The most recent organic composition information available for this category is is the Los Angeles County APCD inventory for 1965, (see Table 3-30). However, the organic composition of this category probably did not undergo significant changes due to APCD Rule 66, [23], [27]. It seems reasonable to assume that the percentage contribution of the various organic types is still as indicated by Table 3-30.

TABLE 3-29 ESTIMATED COMPOSITION OF THE ORGANICS EMITTED BY FLEXIGRAPHIC PRINTING [32]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{6+}-paraffins		Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone	10			N-alkyl ketones	8	Cellosolve acetate	73	Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol	9								
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	19	TOTAL CLASS II	0	TOTAL CLASS III	8	TOTAL CLASS IV	73	TOTAL CLASS V	0

TABLE 3-30. ORGANIC EMISSION COMPOSITION FOR RUBBER, PLASTIC, PUTTY, AND ADHESIVE MANUFACTURING (1965 LA APCD DATA) [33]

COMPOUND TYPE	CONTRIBUTION TO TOTAL EMISSIONS (% by Weight)
Aliphatic Hydrocarbons	51%
Aromatic Hydrocarbons	10%
Alcohols	7%
Ketones	10%
Halogenated Hydrocarbons	5%
Esters and Ethers	1%
Others	16%

In the absence of any definative hydrocarbon composition data, it was necessary to make reasonable estimates of the compounds comprising the categories shown in Table 3-30. It should be noted that these are working estimates only and are based on what seems reasonable and not on actual measurements. Table 3-31 shows how the estimates were made. It should be noted that the uncertainty associated with the estimated composition of the "others" category, is quite large.

The organic composition according to the 5-Class reactivity scheme is shown in Table 3-32.

Pharmaceutical Manufacturing

The present category consists of drug and cosmetic manufacturing. It was not feasible to conduct a survey of the organic emissions from this industry within the level of effort allocated to this study. Also, solvent manufacturers and distributors were unable to supply estimates of the amount of various solvents sold to pharmaceutical manufacturers. The most recent organic composition information available for this industrial category was the Los Angeles County APCD inventory for 1965, [33]. These data are presented in Table 3-33. Since this industry evidently did not undergo significant changes due to APCD Rule 66, it is assumed that the 1965 composition data is still applicable, [31].

TABLE 3-31. ESTIMATED COMPOSITION OF THE ORGANICS EMITTED BY RUBBER, PLASTIC, PUTTY AND ADHESIVE MANUFACTURING OPERATIONS.

Category	Compound Type	Fraction of Each Type	Weight % of Total Hydrocarbons	Actual or estimated Molecular Weight	Mole % of Total Hydrocarbons
Aliphatic Hydrocarbons	Cycloparaffins	0.20	10.2	98 (C_7)	7.5
	C_4+ Paraffins	0.20	10.2	86 (C_6)	8.6
	Olefins	0.60	30.6	56 (C_4)	40.9
			51.0%		
Aromatic Hydrocarbons	Dialkyl benzenes	0.10	1.0	120 (C_9)	0.6
	α-methyl Styrene	0.20	2.0	132 --	1.1
	Styrene	0.70	7.0	118 --	4.4
			10.0%		
Alcohols	Tertiary Alkyl Alcohols	0.30	2.1	88 (C_5)	1.7
	Primary and Secondary Alcohols	0.70	4.9	88 (C_5)	4.2
			7.0%		
Ketones	Cyclic Ketones	0.10	1.0	98 (C_6)	0.7
	Acetone	0.30	3.0	58 --	3.8
	N-alkyl Ketones	0.30	3.0	86 (C_5)	2.6
	Branched Alkyl Ketones	0.30	3.0	114 (C_7)	1.9
			10.0%		
Halogenated Hydrocarbons	Perhalogenated Hydrocarbons	0.20	1.0	320 ($C_3 Cl_8$)	0.2
	Partially Halogenated Hydrocarbons	0.80	4.0	98 ($C_2 Cl_2$)	3.0
			5.0%		
Esters and Ethers	Acetate Esters	1.00	1.0%	72 (C_4)	1.0
			1.0%		
Others	Aliphatic Hydrocarbons	0.50	8.0	58 (C_3)	10.2
	Benzene	0.50	8.0	78 (-)	7.6
			16.0%		100.0%

TABLE 3-32 ESTIMATED COMPOSITION OF THE ORGANICS EMITTED DURING RUBBER, PLASTIC, PUTTY AND ADHESIVE MANUFACTURING [33]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{6+}-paraffins	9	Prim-& sec-alkyl benzenes		Aliphatic olefins	41
Acetylene		Cyclic ketones	1	Cycloparaffins	7	Dialkyl benzenes	1	α-methyl styrene	1
Benzene	7	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones	2	Aliphatic aldehydes	10
Benzaldehyde		2-nitropropane		Styrene	4	Prim-& sec-alkyl alcohols	4	Tri-& tetra-alkyl benzenes	
Acetone	4			N-alkyl ketones	3	Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols	2			Prim-& sec-alkyl acetates	1	Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins	3								
TOTAL CLASS I	16	TOTAL CLASS II	1	TOTAL CLASS III	24	TOTAL CLASS IV	7	TOTAL CLASS V	52

TABLE 3-33. ORGANIC EMISSION COMPOSITION FOR PHARMACEUTICAL MANUFACTURING (1965 LA APCD DATA) [33]

ORGANIC TYPE	CONTRIBUTION TO TOTAL EMISSIONS (% by Weight)
Aliphatic Hydrocarbons	negl.
Aromatic Hydrocarbons	negl.
Alcohols	83%
Ketones	17%
Chlorinated Hydrocarbons	negl.
Esters and Others	negl.

In the absence of any definitive organic composition data, it was necessary to make reasonable estimates of the compounds comprising the categories shown in Table 3-33. It should be noted that these are working estimates only and are based on what seems reasonable and not on actual measurements. Table 3-34 shows the basis for the estimates.

This composition data is presented in the 5-class reactivity scheme in Table 3-35.

Miscellaneous Organic Solvent Operations

The present category consists mostly of miscellaneous chemical production including manufacture of organic chemicals, soaps, cleaners, insecticides, fertilizers, explosives, etc. It also includes miscellaneous solvent usage in industry, in particular the "potting" of electrical and electronic equipment.

Up to date information on the composition of organic emissions from this category is not available. The most recent data are from an LA APCD survey reported in 1965. Table 3-36 summarizes this composition data.

TABLE 3-34. ESTIMATED COMPOSITION OF THE HYDROCARBONS IN PHARMACEUTICAL MANUFACTURING

	Compound Type	Fraction of Each Type	Weight of Total Hydrocarbons	Actual or Estimated Average Molecular Weight	Mole % of Total Hydrocarbons
Ketones	Cyclic Ketones	0.10	1.7	112 (C_7)	1.2
	Acetone	0.30	5.1	58 --	6.7
	N-alkyl Ketones	0.30	5.1	86 (C_5)	4.5
	Branched Alkyl Ketones	0.30	5.1	114 (C_7)	3.4
			17.0%		
Alcohols and Glycol Ethers (Cellosolves)	Methanol	0.10	8.3	32 (-)	19.7
	Tertiary Alkyl Alcohols	0.10	8.3	88 (C_5)	7.2
	Primary and Secondary Alkyl Alcohols	0.80	66.4	88 (C_5)	57.4
			83.0%		100%

TABLE 3-35 ESTIMATED COMPOSITION OF THE ORGANICS EMITTED DURING PHARMACEUTICAL MANUFACTURING [33]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins		Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones	1	Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones	3	Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols	57	Tri-& tetra-alkyl benzenes	
Acetone	7			N-alkyl ketones	5	Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols	7			Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol	20								
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	34	TOTAL CLASS II	1	TOTAL CLASS III	5	TOTAL CLASS IV	60	TOTAL CLASS V	0

TABLE 3-36. COMPOSITION OF ORGANIC EMISSIONS FROM MISCELLANEOUS ORGANIC SOLVENT OPERATIONS [33]

Organic Type	Percentage Contribution (by weight)
Aliphatics	31%
Aromatics	16%
Ketones	27%
Alcohols	15%
Esters	4%
Ethers	3%
Halogenated Hydrocarbons	negl.
Others	4%

The impact which APCD Rule 66 has had on organic composition for this miscellaneous category since 1965 is not known,[23]. Since the composition outlined in Table 3-36 apparently complies with the reactivity criteria of Rule 66, the regulation may not have produced substantial composition changes. Here, it will arbitrarily be assumed that the present composition is the same as in 1965.

The estimated composition of each category of compounds is shown in Table 3-37, with the distribution by the 5-class reactivity scheme shown in Table 3-38.

3.4 MOBILE SOURCES

The sources in this category, include in addition to those sources generally considered to be mobile sources, emissions from miscellaneous gasoline powered equipment such as chain saws, generators, etc.

The major source types included in this category are:

- Light Duty Gasoline Powered Vehicles
- Heavy Duty Gasoline Powered Vehicles
- Other Gasoline Powered Equipment
- Diesel Powered Vehicles
- Aircraft

TABLE 3-37 ESTIMATED COMPOSITION OF THE ORGANICS EMITTED BY MISCELLANEOUS ORGANIC SOLVENT OPERATIONS

	Compound Type	Fraction of Each Type	Weight % of Total Hydrocarbons	Actual or Estimated Molecular Weight	Mole % of Total Hydrocarbons
Aliphatic Hydrocarbons	Cycloparaffins	0.20	6.2	112 (C_7)	4.4
	Olefins	0.20	6.2	112 (C_7)	4.4
	C_4^+ Paraffins	0.60	18.6 31.0%	114 (C_7)	13.1
Aromatic Hydrocarbons	Tri- and Tetra-Alkyl Benzenes	0.10	1.6	134 (C_{10})	1.0
	Prim- and Sec-Alkyl Benzenes	0.30	4.8	106 (C_8)	3.6
	Dialkyl Benzenes	0.60	9.6 16.0%	120 (C_9)	6.4
Ketones	Branched Alkyl Ketones	0.20	5.4	100 (C_6)	4.3
	N-alkyl Ketones	0.30	8.1	72 (C_4)	9.1
	Acetone	0.50	13.5 27.0%	58 (-)	18.7
Alcohols	Tertiary Alkyl Alcohols	0.20	3.0	88 (C_5)	2.7
	Primary- and Secondary- Alkyl Alcohols	0.30	4.5	88 (C_5)	4.1
	Methanol	0.50	7.5 15.0%	32 (-)	18.8
Esters	Prim- and Sec-Alkyl Acetates	1.0	4.0 4.0%	116 (C_6)	2.7
Ethers	Ethers	1.0	3.0 3.0%	88 (C_5)	2.7
Others	Aldehydes	0.2	0.8	86 (C_5)	0.7
	Benzene	0.8	3.2 4.0%	78 (-)	3.3 100%

TABLE 3-38 ESTIMATED DISTRIBUTION OF THE ORGANICS EMITTED BY MISCELLANEOUS ORGANIC SOLVENT OPERATIONS [33]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{6+}-paraffins	13	Prim-& sec-alkyl benzenes	4	Aliphatic olefins	4
Acetylene		Cyclic ketones		Cycloparaffins	4	Dialkyl benzenes	6	α-methyl styrene	
Benzene	3	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones	4	Aliphatic aldehydes	1
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols	4	Tri-& tetra-alkyl benzenes	1
Acetone	19			N-alkyl ketones	9	Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols	3			Prim-& sec-alkyl acetates	3	Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	3
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	44	TOTAL CLASS II	0	TOTAL CLASS III	29	TOTAL CLASS IV	18	TOTAL CLASS V	9

3.4.1 Light Duty Gasoline Powered Vehicles

Exhaust Emissions From Light Duty Gasoline Powered Motor Vehicles

The composition of the organics emitted in the exhaust of gasoline powered automobiles and light trucks depends on a large number of variables. Among the most obvious ones are the composition of the fuel, [36], [37], [38], [39], [40], [41], the type of emission controls [42] and the condition of the car. For example, Table 3-39 shows the effect of fuel composition on the organic composition of the exhaust based on the 5-Class reactivity scheme, [36]. Although the fuels used in these tests are not commercial gasolines, they are mixtures of the types of compounds that are found in commercial gasoline. The significant point is that the exhaust organic composition varies with fuel composition. Similarly, Table 3-40 shows the effect of three categories of emission controls on the composition of the exhaust organic mixture from automobiles burning a leaded premium gasoline, [42].

Any scheme to determine the aggregate exhaust hydrocarbon composition by using a weighted average of tests on individual automobiles is very difficult because of the problems associated with determining an accurate cross section of automobile and control system combinations, exhaust emission rates, various states of operating efficiency, fuel and all of the other variables. Because of these difficulties, it was determined that composition data for hydrocarbon emissions of an aggregate of automobiles which would average out all of the variables, would give the most representative information.

An aggregate sample of this type was obtained by sampling the ambient air in two heavily travelled highway tunnels, [43], [44]. Determining the automobile exhaust hydrocarbon composition by this method is valid for the following reasons:

- Evaporative emissions from moving automobiles are relatively small since emissions from both the carburetor and the fuel tank are vented into the running engine. (A substantial portion of the evaporative emissions occur after the automobile is parked.)

TABLE 3-39 EXHAUST ORGANIC COMPOSITION FOR VARIOUS TYPES OF FUEL MIXTURES [36]

Mole % of Total Exhaust Hydrocarbons

	Isooctane	50% Isooctane 50% 2,4,4 Trimethyl-2-Pentene	2,4,4 Trimethyl -2-Pentene	50% Isooctane 50% m-Xylene	Average
Class I	40	41	46	31	40
Class II	0	0	0	0	0
Class III	21	13	4	13	13
Class IV	0	0	0	29	7
Class V	39	46	50	27	41
	100 %	100 %	100 %	100 %	101 %*

---

* Rounding Error

TABLE 3-40 EXHAUST ORGANIC COMPOSITION FOR VARIOUS TYPES OF EMISSION CONTROL DEVICES [42]

	Mole % of Total Hydrocarbon Emissions			
	Uncontrolled	Modified Combustion*	Air Injection	Average
Class I	34	32	28	31
Class II	0	0	0	0
Clsss III	23	16	19	19
Class IV	10	9	9	9
Class V	33	43	44	40
	100 %	100 %	100%	99% +

* Lean mixture, modified spark timing

+ Rounding Error

For additional composition data see Tables B-12 through B-14.

- Since the exhaust hydrocarbon concentration is high, any ambient or background hydrocarbon component is small.
- The traffic in the two tunnels was limited almost exclusively to gasoline powered vehicles.
- Since the samples were taken in areas which were shielded from the sun, no photochemical reactions could have occurred.

Table 3-41 shows the reactivity classification breakdown for automobile exhaust organic-emissions. The substantial differences between this breakdown and the data in Tables 3-39 and 3-40 are directly attributable to the difficulty in trying to correctly weight each of many variables. The data in the first two tables were obtained from a small number of automobiles under laboratory conditions, whereas the data in Table 3-41 was obtained from a truer cross section of automobile types, under actual driving conditions.

Evaporative Emissions From Light Duty Gasoline Powered Motor Vehicles

There are two significant sources of evaporative emissions from automobiles. (Fuel tank filling and gasoline spillage were reported as gasoline marketing emissions). The first is fuel tank "breathing". Organics are emitted by this process due to changes in the temperature of the fuel tank in a manner similar to that that occurs in underground gasoline storage tanks. The other major source is evaporation of gasoline from the carburetor bowl after the engine is turned off but while the carburetor and surrounding areas are still warm. Evaporation from the carburetor is limited to the so-called "heat soak" period after the engine has been turned off. Vent gases from the carburetor bowl are routed into the engine while it is running, [16].

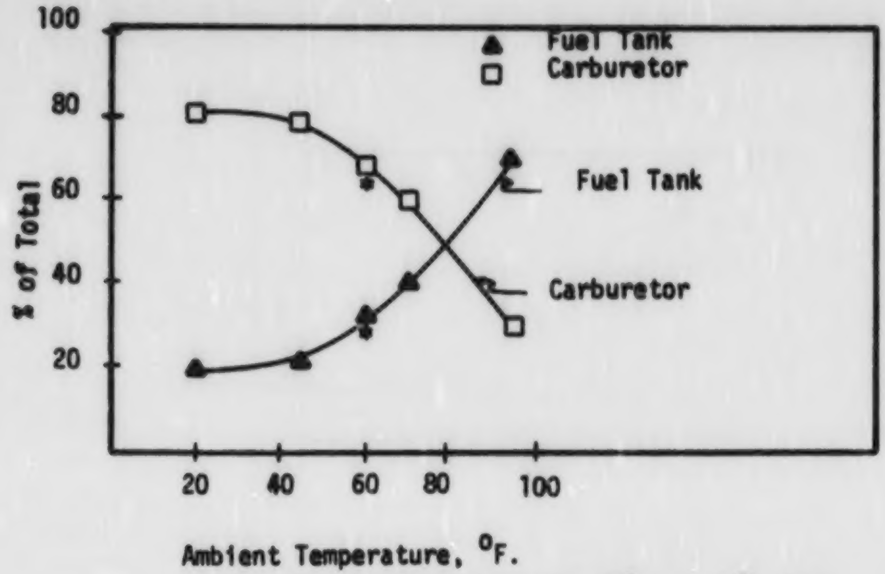
The ratio of the amounts of organics emitted from each of these two sources varies strongly with the ambient temperature. As shown in Figure 3-1 below about 80°F, evaporation from the carburetor predominates, while above that temperature fuel tank breathing is the major contributor. Similarly, Figure 3-2 shows that at a temperature below about 90°F, a very large fraction of the total automotive emissions (the sum of evaporative

TABLE 3-41 COMPOSITION OF THE ORGANICS EMITTED IN THE EXHAUST FROM LIGHT DUTY GASOLINE POWERED VEHICLES [43]

MOLE %

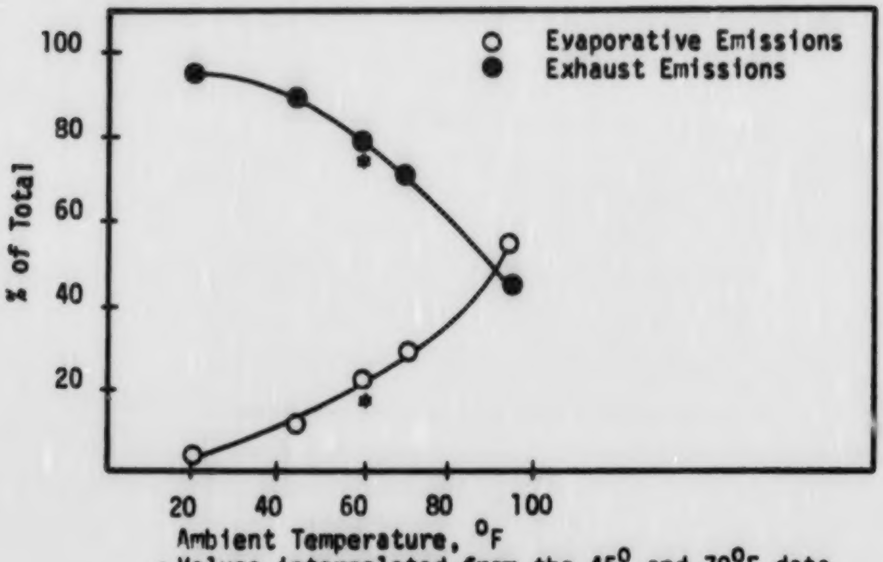
CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	14	Mono-tert-alkyl benzenes		C_{4+}-paraffins	30	Prim-& sec-alkyl benzenes	6	Aliphatic olefins	20
Acetylene	11	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	13	α-methyl styrene	
Benzene	3	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	3
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	28	TOTAL CLASS II	0	TOTAL CLASS III	30	TOTAL CLASS IV	19	TOTAL CLASS V	23

For complete composition data see Table B-15.



Values interpolated from the 45° and 70°F data

Figure 3-1 Change in the Relative Emissions from the Carburetor and Fuel Tank with Ambient Temperature, [16].



* Values interpolated from the 45° and 70°F data

Figure 3-2 Change in the Relative Emissions from Evaporative Sources and Exhaust Gases with Ambient Temperature, [42].

and exhaust emissions) are attributable to exhaust emissions, whereas above that temperature, the evaporative emissions begin to predominate. These data were estimated from 16 automobiles whose model years encompass approximately the years 1967-1969, [42].

Because of these factors it was necessary to estimate the yearly average temperature in the Los Angeles area. For this purpose, an annual average temperature of 60°F was chosen. This temperature is normal for that area, and it was assumed that 1972 was a normal year as far as average temperature is concerned, [18], [19]. Note that this temperature is used in two ways, (1) to determine the ratio between the mass of the evaporative emissions originating at the fuel tank and those originating at the carburetor, and (2) to determine the composition of the fuel tank emissions which varies with temperature (the composition of the emissions from the carburetor are not temperature dependent since it is assumed that whole gasoline is evaporated). Further note that the selection of this temperature in no way affects the estimate of the mass of hydrobarbons emitted; the mass emissions estimates were arrived at by an entirely different method (see Section 2.0).

In order to estimate the composition of the hydrocarbon mixture emitted due to fuel tank breathing, a determination of the average fuel tank temperature had to be made. This was done by adding 10° to the ambient temperature since the actual temperature of the fuel tank would be expected to run slightly higher than ambient due to agitation of the liquid, heat transmission from the warm parts of the car, etc., [16].

Table 3-42 shows a breakdown of the relative amounts of hydrocarbons emitted from both evaporative and exhaust souces.

Table 3-43 shows the data obtained from measurements of the equilibrium vapor over liquid gasoline at 79-80°F. Although these temperatures are about 10° higher than the expected temperature at which tank breathing losses occur, it was assumed the composition of the equilibrium vapors does not vary significantly between the two temperatures and that the higher temperature data would give a sufficiently accurate representation of the true composition. The same table also shows how the composition of the equilibrium vapors does vary between 79-80°F and 85°F, the only

TABLE 3-42 RATIO OF EVAPORATIVE TO EXHAUST ORGANIC EMISSIONS [16]

	Weight % Relative to Evaporative Hydrocarbon Emissions	Weight % Relative to Sum of Evaporative and Exhaust Organic Emissions
45°F		
Carburetor	78.0	9.2
Fuel Tank	22.0	2.6
Exhaust	850	88.3
60°F *		
Carburetor	67.4	14.2
Fuel Tank	32.6	7.9
Exhaust	550	78.0
70°F		
Carburetor	60.4	17.5
Fuel Tank	39.6	11.4
Exhaust	350	71.1

* See Figures 3-1 and 3-2;Interpolated between 45° and 70°F

TABLE 3-43 EQUILIBRIUM VAPORS OVER LOS ANGELES AREA GASOLINES [14]

	Regular Grade Gasoline, Mole %		Premium Grade Gasoline, Mole %	
	80°F	85°F	79°F	85°F
Class I	5	5	3	2
Class II	0	0	0	0
Class III	66	67	78	80
Class IV	3	2	4	3
Class V	26	26	15	15
	100%	100%	100%	100%

For additional composition data see Tables B-2 through B-7.

two temperatures for which data of this type are available. Note that, although the composition varies considerably between regular and premium grades, the variation in the composition with temperature for each grade is small.

In order to estimate the composition of the hydrocarbon emissions from the heat soaking of the carburetor, it was assumed that the emissions were best represented by assuming that whole gasoline was evaporated, [15], [45]. This seems reasonable in light of the fact that the gasoline in the carburetor bowl is subjected to high temperatures for a relatively long period of time.

Table 3-44 shows the composition, by class, of the organic emissions expected from the carburetor and fuel tank.

Composition data on total automotive evaporative emissions is presented in Table 3-45. This data is weighted to account for two parameters: (1) about 1/3 of evaporative emission originates from the carburetor and 2/3 from the fuel tank and, (2) approximately 30% of the gasoline involved in these emissions was regular grade and 70% was premium grade, [15], [16]. (The fraction of regular grade gasoline consumed increased after 1972 until in early 1975 it accounted for about 45% of the gasoline sold; this trend is expected to continue as increasing numbers of automobiles are sold that burn regular grade gasoline, [15].

3.4.2 Heavy Duty Gasoline Powered Vehicles

Exhaust Emissions from Heavy Duty Gasoline Powered Motor Vehicles

The vehicles in this category consist primarily of large trucks and buses. Since no information regarding the composition of the hydrocarbons emitted by this type of vehicle was available, it was assumed that the composition was identical to that for light duty vehicles (cars and light trucks). Since there is no fundamental difference between the engines and fuel used by these types of vehicles, the assumption seems to be a reasonable one.

Therefore, the hydrocarbon composition breakdown for heavy duty gasoline powered vehicles shown in Table 3-46 is identical to that for light duty vehicles.

TABLE 3-44 COMPOSITION OF HYDROCARBON EMISSIONS FROM AUTOMOBILE CARBURETORS AND FUEL TANKS [16]

	Carburetor(a,b) Emissions	% of Total(c) Evaporative Emissions	Fuel tank(d,b) Emissions	% of Total(c) Evaporative Emissions
Class I	5	67%(e)	3	33%(e)
Class II	0		0	
Class III	50		75	
Class IV	30		4	
Class V	15		18	

(a) Composition data based on evaporation of whole gasoline, [15], [45].

(b) Weighted to represent 30% regular grade and 70% premium grade gasoline,[15], [16].

(c) Based on emissions from 16 automobiles using premium grade gasoline,[42].

(d) Composition data for equilibium vapor over whole gasoline at 79°-80°F, [14].

(e) Average annual ambient temperature estimated to be 60°F, [18], [19].

Evaporative Emissions from Heavy Duty Gasoline Powered Vehicles

Since the fuels and fuel systems used in heavy duty gasoline powered vehicles are fundamentally the same as that for light duty vehicles, the evaporative emissions were presumed to be identical to those from light duty vehicles.

Table 3-47 shows the composition of the evaporative emissions from heavy duty gasoline powered vehicles.

3.4.3 Other Types of Gasoline Powered Equipment

Exhaust Emissions from Other Types of Gasoline Powered Equipment

As in the case of heavy duty gasoline powered vehicles, a lack of other information made it necessary to assume that the composition of the exhaust emissions from other types of gasoline powered equipment (motorcycles, chain saws, etc.) is the same as that for light duty motor vehicles.

TABLE 3-45 COMPOSITION OF THE EVAPORATIVE EMISSIONS FROM LIGHT DUTY GASOLINE POWERED VEHICLES [14], [16], [42]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	1	Mono-tert-alkyl benzenes		C_{4+}-paraffins	57	Prim-& sec-alkyl benzenes	9	Aliphatic olefins	13
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	12	α-methyl styrene	
Benzene	4	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	3
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	5	TOTAL CLASS II	0	TOTAL CLASS III	58	TOTAL CLASS IV	21	TOTAL CLASS V	16

Weighted to represent: (1) 67% carburetor, 33% fuel tank emissions;
(2) 30% regular, 70% premium grade gasolines.

TABLE 3-46 COMPOSITION OF THE ORGANICS EMITTED IN THE EXHAUST FROM HEAVY DUTY GASOLINE POWERED MOTOR VEHICLES [43]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	14	Mono-tert-alkyl benzenes		C_{4+}-paraffins	20	Prim-& sec-alkyl benzenes	6	Aliphatic olefins	20
Acetylene	11	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	13	α-methyl styrene	
Benzene	3	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	3
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	28	TOTAL CLASS II	0	TOTAL CLASS III	20	TOTAL CLASS IV	19	TOTAL CLASS V	23

TABLE 3-47 COMPOSITION OF THE EVAPORATIVE EMISSIONS FROM HEAVY DUTY GASOLINE POWERED VEHICLES [14], [16], [42]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	1	Mono-tert-alkyl benzenes		C_{4+}-paraffins	57	Prim-& sec-alkyl benzenes	9	Aliphatic olefins	13
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	12	α-methyl styrene	
Benzene	4	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	3
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	5	TOTAL CLASS II	0	TOTAL CLASS III	58	TOTAL CLASS IV	21	TOTAL CLASS V	16

TABLE 3-48 COMPOSITION OF THE ORGANICS EMITTED IN THE EXHAUST OF OTHER TYPES OF GASOLINE POWERED EQUIPMENT [43]

Mole %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	14	Mono-tert-alkyl benzenes		C_{4+}-paraffins	30	Prim-& sec-alkyl benzenes	6	Aliphatic olefins	20
Acetylene	11	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	13	α-methyl styrene	
Benzene	3	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	3
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	28	TOTAL CLASS II	0	TOTAL CLASS III	30	TOTAL CLASS IV	19	TOTAL CLASS V	23

TABLE 3-49 COMPOSITION OF THE EVAPORATIVE EMISSIONS FROM OTHER GASOLINE POWERED EQUIPMENT [14], [16], [42]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	1	Mono-tert-alkyl benzenes		C_{4+}-paraffins	57	Prim-& sec-alkyl benzenes	9	Aliphatic olefins	13
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	12	α-methyl styrene	
Benzene	4	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	3
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	5	TOTAL CLASS II	0	TOTAL CLASS III	58	TOTAL CLASS IV	21	TOTAL CLASS V	16

Table 3-48 shows the assumed composition of the organics emitted in the exhaust from other types of gasoline powered equipment.

Evaporative Emissions from Other Types of Gasoline Powered Equipment

Since the fuels burned by other types of gasoline powered equipment are similar to the fuels burned by light duty gasoline powered motor vehicles, the assumption was made that the composition of the evaporative emissions was the same.

Table 3-49 shows the estimated composition of the organics emitted due to evaporation from other types of gasoline powered equipment.

3.4.4 Diesel Powered Vehicles

A very comprehensive study of diesel emission composition data has been conducted, in which the authors, by critically evaluating available data, were able to compile a detailed picture of diesel emissions, [46]. The list shown in Table 3-50 (essentially taken directly from that reference) was compiled by considering 2- and 4-cycle diesel engines at a variety of loads and burning a variety of diesel fuels.

It is interesting to note in Table 3-51, that the paraffin component of the exhaust is very similar to the paraffin component of typical diesel fuels. It has, in fact, been found that the composition of diesel fuel is quite similar to diesel exhaust except for low molecular weight components, [47] (for example, there is no methane in diesel fuel).

When these composition estimates are put into the 2-class reactivity scheme, the emissions are shown to be "67% reactive" (by weight). This differs substantially from the 99% value which is generally used. It is not clear why this is so, although the basis for the lower value is well documented, in this report, and the basis for the higher value is, apparently, not well documented. Since the basis for the 67% value is clear, it seems reasonable to assume that it is the more correct.

TABLE 3-50. DIESEL ENGINE EXHAUST HYDROCARBON COMPOSITION [46]

Carbon Number	Compound or Compound Type	Actual or Estimated Molecular Weight	Volume % (Assumed to Equal Mole %)
C_1	Methane	16	10.8
C_2	Acetylene	26	2.2
C_2	Ethylene	28	19.4
C_3	Propylene	42	3.6
C_4	Isobutene	56	1.4
C_5	Pentene	70	0.6
C_6	Hexane	86	0.0
C_6	Benzene	78	0.0
C_7	Heptane	100	0.2
C_7	Toluene	92	0.2
C_8*	Saturate	114	0.0
C_8*	Olefin	112	0.0
C_8*	Aromatic	106	0.0
C_9	Saturate	128	0.9
C_9	Olefin	126	0.1
C_9	Aromatic	120	0.2
C_{10}	Saturate	142	1.2
C_{10}	Olefin	140	0.1
C_{10}	Aromatic	128	0.3
C_{11}	Saturate	156	2.3
C_{11}	Olefin	154	0.1
C_{11}	Aromatic	142	0.6

TABLE 3-50. DIESEL ENGINE EXHAUST HYDROCARBON COMPOSITION [46] (Continued)

Carbon Number	Compound or Compound Type	Actual or Estimated Molecular Weight	Volume % (Assumed to Equal Mole %)
C_{12}	Saturate	170	3.8
C_{12}	Olefin	168	0.2
C_{12}	Aromatic	156	0.9
C_{13}	Saturate	184	2.9
C_{13}	Olefin	182	0.2
C_{13}	Aromatic	170	0.7
C_{14}	Saturate	198	2.9
C_{14}	Olefin	196	0.2
C_{14}	Aromatic	184	0.7
C_{15}	Saturate	212	2.5
C_{15}	Olefin	210	0.1
C_{15}	Aromatic	198	0.6
C_{16}	Saturate	226	2.1
C_{16}	Olefin	224	0.1
C_{16}	Aromatic	212	0.4
C_{17}	Saturate	240	1.4
C_{17}	Olefin	238	0.1
C_{17}	Aromatic	226	0.4
C_{18}	Saturate	254	1.1
C_{18}	Olefin	252	0.1
C_{18}	Aromatic	240	0.3

TABLE 3-50. DIESEL ENGINE EXHAUST HYDROCARBON COMPOSITION [46] (Continued

Carbon Number	Compound or Compound Type	Actual or Estimated Molecular Weight	Volume % (Assumed to Equal Mole %)
C_{19}	Saturate	268	0.8
C_{19}	Olefin	266	0.0
C_{19}	Aromatic	254	0.2
C_{20}	Saturate	282	0.8
C_{20}	Olefin	280	0.0
C_{20}	Aromatic	268	0.2
C_{21}	Saturate	296	0.4
C_{21}	Olefin	294	0.0
C_{21}	Aromatic	282	0.1
C_{22}	Saturate	310	0.2
C_{22}	Olefin	308	0.0
C_{22}	Aromatic	296	0.0
C_1	Formaldehyde	30	15.2
C_5	Alphatic Aldehydes (Average Composition assumed to be C_5)	86	15.2
C_3	Acrolein (Propene Aldehyde)	56	1.2
			100%

*For C_8 and higher hydrocarbons the following distribution was assumed by Ref.[46], 77% saturates, 4% olefins, and 19% aromatics, all volume %.

+ Two-ring systems assumed for C_{10} and higher aromatics

TABLE 3-51. COMPARISON OF DIESEL FUEL COMPOSITION AND THE COMPOSITION OF DIESEL EXHAUST HYDROCARBONS

	Weight %	
Compound Type	Diesel Fuel Composition, [48]	Diesel Exhaust Hydrocarbon Composition, [46]
Paraffins	60-85 %	85% (a)
Straight Chain and Branched Paraffins	30-40 %	
Napthenes	25-45 %	
Olefins	1-10 %	14 % (b)
Aromatics	15-40 %	1 % (c)

(a) Molecular weight assumed to be 140

(b) Molecular Weight 41

(c) Molecular weight assumed to be 180

TABLE 3-52. ORGANIC COMPOSITION OF THE EXHAUST FROM DIESEL POWERED VEHICLES [46]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	11	Mono-tert-alkyl benzenes		C_{4+}-paraffins	24	Prim-& sec-alkyl benzenes	1	Aliphatic olefins	27
Acetylene	2	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	5	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	30
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	13	TOTAL CLASS II	0	TOTAL CLASS III	24	TOTAL CLASS IV	6	TOTAL CLASS V	57

The composition data are presented in the 5-class reactivity format in Table 3-52.

As shown in Table 1-3, the photochemical reactivity of diesel exhaust is considerably higher than of gasoline powered vehicle exhaust. This is the effect of, primarily, a higher fraction of class V compounds, as shown in Table 3-53. This seems to conflict with the generally held view that diesels are "cleaner" than conventional power plants. However, Table 3-54 shows that although the reactivity of diesel exhaust is higher than that of gasoline powered vehicles, the mass emission rate, on a per mile basis, is much lower.

TABLE 3-53. COMPARISON OF THE ORGANIC EMISSIONS FROM GASOLINE AND DIESEL POWERED VEHICLES *

	Mole %	
	Gasoline	Diesel
Class I	28	0
Class II	0	0
Class III	30	24
Class VI	19	6
Class V	23	57

*See Table 1-3

TABLE 3-54. COMPARISON OF THE MASS HYDROCARBON EMISSION RATES FROM DIESEL POWERED VEHICLES AND GASOLINE POWERED PASSENGER CARS [49]

	Diesel (gm/mi)	Gasoline (gm/mi)
Hydrocarbons	0.29	2.68
Formaldehyde	0.015	0.075
Aliphatic Aldehydes (as CH_2O)	0.020	0.082
Acrolein	0.013	0.060

3.4.5 Aircraft

Jet Aircraft

The organic emission characteristics of gas turbine (jet) powered aircraft are unusual in two major respects. First, the organic emission rate (lbs/hr) is highest at the lowest fuel flow rate, whereas for most combustion devices the reverse is most often true, [50], [51]. Second, the low power, idle mode is used for the majority of the time the engines are running and the aircraft is in the Los Angeles basin.

Table 3-55 shows the relative emission rates and the time in each operating mode for a typical landing-takeoff cycle, [52]. According to the table almost all of the emissions occur during the taxi-idle portion of the cycle. This indicates that hydrocarbon composition data obtained at the idle power setting would be a very good approximation of the composition of the total hydrocarbons emitted by gas turbine engines during the time that the aircraft is in the air basin. This period excludes most of the climb and approach and all of the cruise portion of the flight.

TABLE 3-55 FRACTION OF HYDROCARBON EMISSIONS OCCURRING IN EACH OPERATING MODE

Mode	Relative Emission Rate, [53]	Minutes in Each Mode, [52]	% of Total* Organics Emitted in Each Operating Mode
Taxi-idle	16.2	26	98%
Takeoff-climbout	1.2	3	1%
Approach	1.0	4	1%
			100%

* These percentages apply to the organic emissions occurring in the vicinity of the airport and consequently excluded emissions that occur during the high altitude, en route phase of the flight.

Table 3-56 shows the distribution of organics in the exhaust of a turbine engine. These data are assumed to be representative of gas turbine engines in general since it is known that the composition of the hydrocarbons tend not to vary substantially from turbine to turbine, [50], although the mass emission rate does, [54]. Note that the hydrocarbons are distributed only by carbon number (i.e., number of carbon atoms in the molecule and not by compound type). The overall mole fraction of aldehydes are, however, shown. This set of data was chosen in the absence of any definitive hydrocarbon emission study, [50].

Since these data are the most detailed available, it was necessary to make a working approximation of the composition of the compounds associated with each carbon number. These approximations were made on the basis of what seemed reasonable; there is, however, no data available to verify them. These approximations are shown in Table 3-57. Note that in all three cases, the total aldehyde fraction nearly matches the measured values as shown in Table 3-56. Table 3-58 shows the variation in hydrocarbon emissions for each class of compounds with variation in operating mode.

TABLE 3-56. DISTRIBUTION OF THE ORGANICS IN GAS TURBINE EXHAUST, [53]

	Mole % of Total Organics					
CARBON NUMBER	IDLE		TAKEOFF		APPROACH	
1	2	11	3	3	3	5
2	6		0		1	
3	3		0		1	
4	2	11	1	5	1	5
5	2		3		2	
6	7		1		2	
7	8	38	1	33	7	33
8	7		13		14	
9	11		6		2	
10	12		13		10	

TABLE 3-56. DISTRIBUTION OF THE ORGANICS IN GAS TURBINE EXHAUST [53] (Continued)

11	9	40	5	59	5	57
12	8		4		4	
13	7		4		3	
14	5		5		4	
15	3		3		4	
16	2		3		3	
17	1		4		4	
18	1		3		3	
19+	4		30		27	
Weight % Aldehydes relative to total hydrocarbons	10%		30%		57%	
Relative mass emission rate	16.2		1.2		1.0	

TABLE 3-57. APPROXIMATE DISTRIBUTION OF ORGANIC TYPES BY CARBON NUMBER CATEGORY

		Mole %		
Carbon Number Category	Type of Compounds	Taxi-idle Mode	Takeoff Mode	Approach Mode
1-3	Paraffins	7	2	1
	Acetylene	1	0	0
	Olefins	2	0	1
	Aldehydes	1	1	3
4-6	Paraffins	7	2	1
	Olefins	2	1	0
	Aldehydes	1	2	3
	Benzene	1	0	1

TABLE 3-57. APPROXIMATE DISTRIBUTION OF ORGANIC TYPES BY CARBON NUMBER CATEGORY (Continued)

7-10	Paraffins	19	17	17
	Olefins	7	7	3
	Aldehydes	4	3	7
	Primary and Secondary alkyl benzenes	4	3	3
	Dialkyl Benzene	4	3	3
11+	Paraffins	12	6	23
	Olefins	8	12	6
	Aldehydes	4	17	17
	Mono.Tertiary benzene	4	6	0
	Primary and Seconday alkyl benzenes	4	6	5
	Dialkyl benzenes	4	6	6
	Tri-and Tetra-alkyl benzenes	4	6	0
		100%	100%	100%

TABLE 3-58 VARIATIONS IN THE COMPOSITION OF THE ORGANIC EMISSIONS FROM GAS TURBINE (JET) AIRCRAFT ENGINES WITH POWER SETTING [53]

	Taxi-idle mode	Takeoff-Climbout mode	Approach mode
Class I	9	2	2
Class II	4	6	0
Class III	38	25	41
Class IV	16	18	17
Class V	33	49	40
	100%	100%	100%

Table 3-59 shows the composition of gas turbine exhaust organics. These data were derived from Table 3-57 and weighted to account for the fraction of time spent in each operating mode. Note that the aliphatic aromatic ratio is about two to one, which agrees well with data from two other jet engines at a total of five different power settings, [50].

Although the fuels used in diesels and jet engines are chemically similar, it would be expected that the composition of the exhaust hydrocarbons would be substantially different due to the fundamental differences in the combustion processes. In a diesel engine the fuel can continue to burn for some time after the combustion products leave the combustion cylinder. This would tend to result in lower molecular weight hydrocarbons being emitted since the combustion would be more complete. In a gas turbine, however, the hot combustion products must be cooled prior to passing through the turbine blades. This is done by quenching the exhaust gases with several volumes of relatively cool ambient air. Since this lowers the temperature well below the temperature at which combustion can occur, combustion effectively stops.

Piston Aircraft

Since reciprocating aircraft engines are fundamentally similar to gasoline powered automobile engines, and since the fuel burned is similar, it is expected that the composition of the hydrocarbons emitted would, likewise, be similar. However, since aircraft engines are not subject to emission controls, if automotive emissions were to be used to model aircraft emissions, the lack of such controls had to be considered.

The organic composition data presented in Table 3-60 is the same as that for an uncontrolled automobile engine, [55]. Since reciprocating aircraft engines contribute a very small fraction of the total hydrocarbon emissions, the effect of any errors that result from using the automotive approximation is also small.

TABLE 3-59 ORGANIC EMISSIONS FROM GAS TURBINE ENGINES [50], [53]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	7	Mono-tert-alkyl benzenes	4	C_{4+}-paraffins	38	Prim-& sec-alkyl benzenes	8	Aliphatic olefins	19
Acetylene	1	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	8	α-methyl styrene	
Benzene	1	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	10
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	4
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	9	TOTAL CLASS II	4	TOTAL CLASS III	38	TOTAL CLASS IV	16	TOTAL CLASS V	33

For additional data see Tables B-16 through B-18.

TABLE 3-60 COMPOSITION OF THE ORGANICS EMITTED IN PISTON AIRCRAFT ENGINE EXHAUST (AS APPROXIMATED BY UNCONTROLLED AUTOMOTIVE EMISSIONS) [55]

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	20	Mono-tert-alkyl benzenes		C_{4+}-paraffins	22	Prim-& sec-alkyl benzenes	6	Aliphatic olefins	31
Acetylene	12	Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	4	α-methyl styrene	
Benzene	2	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	2
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	34	TOTAL CLASS II	0	TOTAL CLASS III	23	TOTAL CLASS IV	10	TOTAL CLASS V	33

3.5 DATA SUMMARY

The data presented in this chapter are subject to some limitations which should be well understood before they are used for any other purposes:

- The data, in the strictest sense, apply only to the Los Angeles AQCR; how the composition of the emissions from each source type vary from one region to another is not known.
- Some of the composition data are quite old.
- Some of the data are estimates and not actual test results.

Tables 3-61 through 3-63 summarize the organic composition data for 2-Class, 5-Class and 6-Class reactivity schemes. In the 2-Class scheme, the mole percent of compounds from stationary sources that fall in Class I (unreactive) range from 0% to 100%. If the dry cleaning and degreasing categories are omitted, the range is 4% to 90%. (The emissions from dry cleaning and degreasing are unusual in that they are very simple mixtures which contain only one or two classes of compounds). Conversely, the reactive components comprise 10% to 96% of the total on a mole basis. There does not appear to be any valid generalization regarding the fraction of the hydrocarbons that are reactive for stationary sources.

The reactive mole fraction for mobile sources ranges from 67% to 95%. The range for exhaust emissions from gasoline powered vehicles and equipment and diesel powered vehicles is 72% to 87% reactive mole fraction.

In the summary of the 5- and 6- Class schemes, the most notable feature is the very small fraction of compounds, from all sources, that fall into Class II of these schemes.

The mole fraction of methane for all sources varies from 0% to 78% With the exception of petroleum production, fuel combustion, and waste burning, the maximum fraction is 11%. The result is, that with the exception of these three source types, there are only very small differences between the 5- Class and the 6- Class reactivity schemes.

TABLE 3-61 DISTRIBUTION OF ORGANIC COMPOUNDS IN A 2-CLASS REACTIVITY SCHEME

	Mole %	
SOURCE CATEGORY	CLASS I	CLASS II
STATIONARY SOURCES - FUELS AND COMBUSTION		
Petroleum Production & Refining		
Petroleum Production	84	16
Petroleum Refining	11	89
Gasoline Marketing		
Underground Gasoline Storage Tanks	18	82
Automobile Gasoline Tank Filling	4	96
Fuel Combustion	90	10
Waste Burning & Other Fires	74	26
STATIONARY SOURCES - ORGANIC CHEMICALS		
Surface Coating		
Heat Treated	20	80
Air Dried	14	86
Dry Cleaning		
Petroleum Based Solvents	0	100
Synthetic Solvent (PCE)	100	0
Degreasing		
TCE Solvent	0	100
1,1,1-T Solvent	100	0
Printing		
Rotogravure	16	84
Flexigraphic	19	81
Industrial Process Sources		
Rubber & Plastic Manufacturing	16	84
Pharmaceutical Manufacturing	34	66
Miscellaneous Chemical Manufacturing	44	56
MOBILE SOURCES		
Light Duty Gasoline Powered Vehicles		
Exhaust Emissions	28	72
Evaporative Emissions	5	95
Heavy Duty Gasoline Powered Vehicles		
Exhaust Emissions	28	72
Evaporative Emissions	5	95
Other Gasoline Powered Equipment		
Exhaust Emissions	28	72
Evaporative Emissions	5	95
Diesel Powered Vehicles	13	87
Aircraft		
Jet	9	91
Piston	34	66

TABLE 3-62 DISTRIBUTION OF ORGANIC COMPOUNDS IN A 5-CLASS REACTIVITY SCHEME

SOURCE CATEGORY	Mole %				
	CLASS I	CLASS II	CLASS III	CLASS IV	CLASS V
STATIONARY SOURCES - FUELS AND COMBUSTION					
Petroleum Production & Refining					
Petroleum Production	84	0	16	0	0
Petroleum Refining	11	0	67	8	14
Gasoline Marketing					
Underground Gasoline Storage Tanks	18	0	60	0	22
Automobile Gasoline Tank Filling	4	0	69	9	18
Fuel Combustion	90	0	3	1	6
Waste Burning & Other Fires	74	0	7	3	16
STATIONARY SOURCES - ORGANIC CHEMICALS					
Surface Coating					
Heat Treated	20	0	28	50	2
Air Dried	14	0	52	29	5
Dry Cleaning					
Petroleum Based Solvents	0	0	94	5	1
Synthetic Solvents	100	0	0	0	0
Degreasing					
TCE Solvent	0	0	0	100	0
1,1,1-T Solvent	100	0	0	0	0
Printing					
Rotogravure	16	0	61	23	0
Flexigraphic	19	0	8	73	0
Industrial Process Sources					
Rubber & Plastic Manufacturing	16	1	24	7	52
Pharmaceutical Manufacturing	34	1	5	60	0
Miscellaneous Chemical Manufacturing	44	0	29	18	9
MOBILE SOURCES					
Light Duty Gasoline Powered Vehicles					
Exhaust Emission	28	0	30	19	23
Evaporative Emissions	5	0	58	21	16
Heavy Duty Gasoline Powered Vehicles					
Exhaust Emissions	28	0	30	19	23
Evaporative Emissions	5	0	58	21	16
Other Gasoline Powered Equipment					
Exhaust Emissions	28	0	30	19	23
Evaporative Emissions	5	0	58	21	16
Diesel Powered Vehicles	13	0	24	6	57
Aircraft					
Jet	9	4	38	16	33
Piston	34	0	23	10	33

TABLE 3-63 DISTRIBUTION OF ORGANIC COMPOUNDS IN A 6-CLASS REACTIVITY SCHEME

SOURCE CATEGORY	Mole %					
	CLASS 0 (CH_4)	CLASS I	CLASS II	CLASS III	CLASS IV	CLASS V
STATIONARY SOURCES - FUELS AND COMBUSTION						
Petroleum Production & Refining						
Petroleum Production	64	20	0	16	0	0
Petroleum Refining	2*	9	0	67	8	14
Gasoline Marketing						
Underground Gasoline Storage Tanks	3	15	0	60	0	22
Automobile Gasoline Tank Filling	0	4	0	69	9	18
Fuel Combustion	78	12	0	3	1	6
Waste Burning & Other Fires	59	15	0	7	3	16
STATIONARY SOURCES - ORGANIC CHEMICALS						
Surface Coating						
Heat Treated	2	18	0	28	50	2
Air Dried	0	14	0	52	29	5
Dry Cleaning						
Petroleum Based Solvents	0	0	0	94	5	1
Synthetic Solvents	0	100	0	0	0	0
Degreasing						
TCE Solvent	0	0	0	0	100	0
1,1,1-T Solvent	0	100	0	0	0	0
Printing						
Rotogravure	0	16	0	61	23	0
Flexographic	0	19	0	8	73	0
Industrial Process Sources						
Rubber & Plastic Manufacturing	0	16	1	24	7	52
Pharmaceutical Manufacturing	0	34	1	5	60	0
Miscellaneous Chemical Manufacturing	0	44	0	29	18	9
MOBILE SOURCES						
Light Duty Gasoline Powered Vehicles						
Exhaust Emissions	10	18	0	30	19	23
Evaporative Emissions	0	5	0	58	21	16
Heavy Duty Gasoline Powered Vehicles						
Exhaust Emissions	10	18	0	30	19	23
Evaporative Emissions	0	5	0	58	21	16
Other Gasoline Powered Equipment						
Exhaust Emissions	10	18	0	30	19	23
Evaporative Emissions	0	5	0	58	21	16
Diesel Powered Vehicles	11	2	0	24	16	47
Aircraft						
Jet	2	7	4	38	16	33
Piston	18	16	0	23	10	33

* Estimated to be 1/3 of the $C_1 - C_3$ paraffin emissions for this category

3.6 REFERENCES

1. Private communication, Robert Murray, Los Angeles County Air Pollution Control District, Los Angeles, California, February 2, 1975.

2. Private communication, James Daley, Standard Oil Company, El Segundo, California, February 12, 1975.

3. Private communication, Sanford Weiss, Los Angeles County Air Pollution District, Los Angeles, California, November 1974; internal document titled "Summary-Survey Questionnaire, Hydrocarbon Emissions."

4. Private communication, E. W. Mertens, Chevron Research Corporation, Richmond, California, February 12, 1975.

5. Private communication, Jack Remnet, Atlantic Richfield Corporation, Wilmington, California, February 12, 1975.

6. Private Communication, Morris Goldberg, Environmental Protection Agency Region IX, San Francisco, California, January 31, 1975.

7. Private communication, Sanford Weiss, Los Angeles County Air Pollution Control District, Los Angeles, California, January 23, 1975.

8. Private communication, Robert Murray, Los Angeles County Air Pollution Control District, Los Angeles, California, January 31, 1975.

9. Profile of Air Pollution - 1971, Los Angeles County Air Pollution Control District, Los Angeles, California, 1971.

10. Air Pollution Engineering Manual, 2nd Ed., John A. Danielson, Environmental Protection Agency, Research Triangle Park, N.C., May 1973.

11. R. L. Martin and J. C. Winters, "Determination of Hydrocarbons in Crude Oil by Capillary-Column Gas Chromatography," Analytical Chemistry, Vol. 35, No. 12, pg. 1930-33, November 1963.

12. A. C. Stern, Air Pollution-Volume 3, 2nd Edition, Chapter 34, Academic Press, New York, 1968.

13. W. N. Sanders and J. B. Maynard, "Capillary Gas Chromatographic Method for Determining C_3-C [sic] Hydrocarbons in Full Range Motor Gasolines," Analytical Chemistry, Vol. 40, No. 3, pg 527-535, March 1968.

14. Private communication, Los Angeles County Air Pollution Control District, November 1974, internal document titled "Liquid and Equilibrium Vapor Analysis (APCD)-Test No. C-1840," August 9, 1972.

15. Private communication, Henry Mayrsohn, California Air Resources Board, El Monte California, January 23, 1975.

16. "Gasoline Modification-Its Potential as an Air Pollution Control Measure in Los Angeles County," joint project, California Air Resources Board, Los Angeles County Air Pollution Control District, and Western Oil and Gas Association, November 1969.

17. John C. Trijonis, An Economic Air Pollution Control Model-Application: Photochemical Smog in Los Angeles County in 1975, Ph.D. Thesis, California Institute of Technology, Pasadena, California, May 1972.

18. Stephen S. Visher, Climatic Atlas of the United States, Harvard University Press, Cambridge, Mass., 1954.

19. Climatic Atlas of the United States, U. S. Department of Commerce, June 1968.

20. Private communication, Howard W. Linnard, California State Air Resources Board, March 1975.

21. M. R. Brunelle, J. E. Dickinson and W. J. Hamming, Effectiveness of Organic Solvents in Photochemical Smog Formation, Los Angeles County Air Pollution Control District, July 1966.

22. Rules and Regulations, Los Angeles County Air Pollution Control District. (no date)

23. Private communication, Sanford Weiss, Los Angeles County Air Pollution Control District, January 1975.

24. Private communication, Charles Finnegan, Ameritone Paint Corporation, Los Angeles, California, January 1974.

25. Private communication, Raymond J. Connor, Assistant Technical Director, National Paint & Coating Association, Washington, D.C., Nov. 5, 1974.

26. Private communication, Fred Thoits, Environmental Protection Agency Region IX, October 1974; data contained in letter from B. A. Thomas, Office Manager, Ashland Chemical Company, Santa Fe Springs, California, dated February 19, 1974.

27. Private communication, William Ellis, Chevron Research Company, El Segundo, California, January 1975.

28. Private communication, Fred Thoits, Environmental Protection Agency Region IX, October 1974; data contained in letter from E. E. Loveland, Region Technical Service Manager, AMSCO Division, Union Oil Company of California, LaMirada, California, dated March 21, 1974, and AMSCO Product Bulletin 140 Solvent 66/3.

29. Private communication, Fred Thoits, Environmental Protection Agency Region IX, October 1974; data contained in letter from Chevron Research Company, El Segundo, California, date unknown.

30. Private communication, Fred Thoits, Environmental Protection Agency Region IX; October 1974, data contained in a document from the Shell Oil Company which gives specifications for solvents distributed west of the Rocky Mountains.

31. Private communication, George Thomas, Los Angeles County Air Pollution Control District, February 1975.

32. Private communication, George Rhett, Los Angeles County Air Pollution Control District, February 1975.

33. Private communication, George Thomas, Los Angeles County Air Pollution Control District, "APCD Organic Solvent Inventory for 1965," February 1975.

34. Private communication, Robert Thomas and Jerry Smernott, Ashland Chemical Company, Santa Fe Springs, California, January 1975.

35. Private communication, E. E. Loveland, Region Technical Service Manager, AMSCO Division of Union Oil Company of California, La Mirada, California, January 1975.

36. R. D. Fleming, "Effect of Fuel Composition of Exhaust Emissions from a Spark-Ignition Engine," U.S. Department of the Interior, Bureau of Mines, Report of Investigations #7423. (no date)

37. E. E. Wigg, R. J. Champion, and W. L. Peterson, "The Effect of Fuel on Hydrocarbon and Oxygenate Emissions," Society of Automotive Engineers Report #720251, presented to the Automotive Engineering Congress, Detroit, Michigan, January 10-14, 1972.

38. B. Dimitriades, B. H. Eccleston, and R. W. Hurn, "An Evaluation of the Fuel Factor Through Direct Measurement of Photochemical Reactivity of Emissions," J. APCA, Vol. 20, No. 3, pg. 150-160, March 1970.

39. J. S. Ninomiya and B. Biggers, "Effects of Toluene Content in Fuel on Aromatic Emissions in the Exhaust," J. APCA, Vol. 20, No. 9, pg. 603-611, September 1970.

40. J. M. Heuss, G. J. Nebel, and B. A. O'Alleva, "Effects of Gasoline Aromatic and Lead Content on Exhaust Hydrocarbon Reactivity," Environmental Science and Technology, Vol. 8, No. 7, pg. 641-647, July 1974.

41. K. T. Dishart and W. E. Harris, "The Effect of Gasoline Hydrocarbon Composition on Automotive Exhaust Emissions," Proc. Am. Petroleum Inst. Div. Refin., Vol 48, pg. 612-642, 1968.

42. W. E. Morris and K. T. Dishart, "Effect of Automotive Emission Requirements on Gasoline Characteristics," ASTM Special Technical Publication 487, pg. 63-93, presented at the Seventy-third Annual Meeting, American Society for Testing and Materials, Toronto, Ontario, Canada, June 21-26, 1970.

43. Private communication, Henry Mayrsohn, California Air Resources Board, El Monte, California, November 1974; results of tests of automotive hydrocarbon emissions in two long highway tunnels.

44. Private communication, Henry Mayrsohn, California Air Resources Board, El Monte, California, January 1975.

45. Private communication, William MacBeth, Los Angeles County Air Pollution Control District, January 23, 1975.

46. C. W. Spicer and A. Levy, "The Photochemical Smog Reactivity of Diesel Exhaust Organics," report to the Coordinating Research Council from Battelle Columbus Laboratories, May 1975.

47. (a) "Chemical Identification of the Odor Components in Diesel Engine Exhaust," Final Report to CRC and PHS, PHS Contract No. PH 22-68-20, CRC Project No. CAPE-7, July 1969,
(b) "Chemical Identification of the Odor Components in Diesel Engine Exhaust," Final Report to CRC and HEW, HEW Contract No. CAP-22-69-63, CRC Project No. CAPE 7-68, June 1970,
(c) "Chemical Identification of the Odor Components in Diesel Engine Exhaust," Final Report to CRC and EPA, EPA Contract No. EHSD 71-18, CRC Project No. CAPE 7-68, June 1971; as reported in Reference 46.

48. Private Communication, P. Levins, Arthur D. Little, Inc., 1974, as reported in Reference 46.

49. K. J. Springer, "Emissions from a Gasoline- and Diesel-Powered Mercedes 220 Passenger Car," report to EPA, Contract No. CPA-70-44, June 1971, as reported in Reference 46.

50. R. H. Groth and D. J. Robertson, "Reactive and Unreactive Hydrocarbon Emissions from Gas Turbine Engines," APCA #74-89, presented at the 67th Annual Meeting of the Air Pollution Control Association, Denver, Colorado, June 9-13, 1974.

51. K. H. Becker and J. Schurath, "Photo-Oxidation of Aircraft Engine Emissions at Low and High Altitudes," Institüt für Physikalisch Chemie der Universität Bonn, W. Germany, AGARD-CP-125.

52. "Compilation of Air Pollution Emission Factors," AP-42, Second Addition, Environmental Protection Agency, April 1973.

53. J. O. Chase and R. W. Hurn, "Measuring Gaseous Emissions from an Aircraft Turbine Engine," SAE #700249, presented at the Society of Automotive Engineers National Air Transportation Meeting, New York, April 20-23, 1970.

54. A. W. Wilson, "Detailed Exhaust Emission Measurements of Three Different Turbofan Engine Designs," AGARD Conference Proceedings, No. 125, April 9-13, 1974, AGARD-CP-125.

55. W. E. Morris and K. T. Dishart, "Influence of Vehicle Emission Control Systems on the Relationship Between Gasoline and Vehicle Exhaust Hydrocarbon Composition," Effect of Automotive Emission Requirements on Gasoline Characteristics, ASTM Special Technical Publication 487, presented at the Seventy-third Annual Meeting American Society for Testing and Materials, Toronto, Ontario, Canada, 21-26 June 1970, pg. 63-94.

Background Material:

Petroleum Refining

R. L. Martin, John C. Winters, and J. A. Williams, "Composition of Crude Oils by Gas Chromatography: Geological Significance of Hydrocarbon Distribution," Proc. 6th World Petrol Congr, Sect V, Paper 13, Frankfurt, Germany, 1963.

I. A. Musayev, et. al., "Investigations of the Chemical Composition of Middle Distillates of Sulphur Bearing Crude Oil of the USSR," Proc. 6th World Petrol. Congr., Sect. V, Paper 21, Frankfurt, Germany, 1963.

L. L. Laster, "Atmospheric Emissions from the Petroleum Refining Industry," Environmental Protection Agency, Research Triangle Park, N.C., August 1973, PB 225-040, EPA-650/2-73-017.

Waste Burning and Other Fires

W. N. Tottle and M. Feldstein, "Gas Chromatographic Analysis of Incinerator Effluents," J. APCA, Vol. 10, No. 6, December 1960.

E. F. Darley, et. al, "Contribution of Burning of Agricultural Waste to Photochemical Air Pollution, J. APCA, Vol. 11, No. 12, December 1966.

R. L. Sterburg, et. al., "Field Evaluation of Combustion Air Effects on Atmospheric Emissions from Municipal Incinerators," J. APCA, Vol. 12, No. 2, February 1962.

R. W. Gerstle and D. A. Kemnitz, "Atmospheric Emissions from Open Burning," J. APCA, Vol. 17, No. 5, May 1967.

R. W. Babel, E. F. Darley, and E. A. Schuck, "Emissions from Burning Grass Stubble and Straw," J. APCA, Vol. 19, No. 7, July 1969.

R. L. Sterburg, et. al., "Effects of High Volatile Fuel on Incinerator Effluents," presented at the 53rd Annual Meeting of APCA, Netherland Hilton Hotel, Cincinnati, Ohio, May 22-26, 1960.

Gasoline Powered Vehicles

Effect of Automobile Emission Requirements on Gasoline Characteristics, ASTM Special Technical Publication 487, a Symposium presented at the Seventy-third Annual Meeting, American Society for Testing and Materials.

B. Dimitriades, B. H. Eccleston, and R. W. Hurn, "An Evaluation of the Fuel Factor Through Direct Measurement of Photochemical Reactivity of Emissions," J. APCA, Vol. 20, No. 3, March 1970.

E. E. Wigg, R. J. Campion, W. L. Peterson, "The Effect of Fuel Hydrocarbon Composition on Exhaust Hydrocarbon and Oxygenate Emissions," Society of Automotive Engineers Paper #720251, presented at the Automotive Engineering Congress, Detroit, Mich.

B. Dimitriades and T. C. Wesson, "Reactivities of Exhaust Aldehydes," U. S. Department of the Interior, Report of Investigations 7527, May 1971.

R. D. Fleming, "Effect of Fuel Composition on Exhaust Emissions from A Spark-Ignition Engine," U. S. Department of Interior, Report of Investigations #7423. (No Date).

J. S. Ninomiya and B. Biggers, "Effects of Toluene Content in Fuel on Aromatic Emissions in the Exhaust," J. APCA, Vol. 20, No. 9, September 1970.

J. M. Heuss, G. J. Nebel, and B. A. D'Alleua, "Effects of Gasoline Aromatic and Lead Content on Exhaust Hydrocarbon Reactivity," Environmental Science and Technology, Vol. 8, No. 7, July 1974.

Diesel Exhaust Emissions

L. R. Reckner, W. E. Scott, and W. F. Biller, "The Composition and Odor of Diesel Exhaust," Proc. of the Amer. Petroleum Institute, 48, 133-144, 1965.

E. W. Landen and J. M. Perez, "Some Diesel Exhaust Reactivity Information Derived by Gas Chromatography," Society of Automotive Engineers 740530, presented at the Combined Commercial Vehicle and Fuels and Lubricants Meetings, Chicago, Illinois, June 17-21, 1974.

H. R. Taliaferro, J. O. Becker, and T. O. Wagner, "Atmospheric Pollution from Diesel Engines," presented at the Seventh World Petroleum Conf., Mexico City, April 1967.

H. C. Lord, et. al., "Measurement of Exhaust Emissions in Piston and Diesel Engines by Dispersive Spectroscopy," J. APCA, Vol. 24, No. 2, February 1974.

4.0 SOURCE REACTIVITY RATINGS AND REACTIVE ORGANIC INVENTORIES

This chapter synthesizes the information presented in previous chapters to derive source reactivity ratings and reactive emission inventories for organic sources in the Metropolitan Los Angeles AQCR. Section 4.1 presents source molar reactivities for each of the 2-, 5-, and 6- group reactivity classification schemes. Section 4.2 gives corresponding source weight reactivities. Finally, Section 4.3 combines the source reactivity ratings with the total organic inventory to arrive at reactive organic inventories according to the 2-, 5-, and 6- group schemes. Each section includes a discussion of the principal features in the numerical results.

4.1 SOURCE MOLAR REACTIVITIES

Table 4-1 lists source molar reactivities for each of the 17 types of stationary sources and 9 types of mobile sources considered in this study. The source molar reactivities are presented for the 2-, 5-, and 6-group reactivity classification schemes. These reactivities have been calculated from the source organic composition data summarized in Table 3-63 and from the reactivity factors for the 2-, 5-, and 6-group schemes listed in Table 1-2. It should be re-emphasized that the reactivities based on the 5- and 6-group schemes are relative, and that the scales for these schemes have been chosen such that auto exhaust retains the same absolute rating for all three classification schemes.

Several features of Table 4-1 deserve special comment. The most important result is that molar reactivities are fairly uniform among

TABLE 4-1. SOURCE MOLAR REACTIVITIES FOR THE 2-, 5-, AND 6- GROUP SCHEMES

SOURCE CATEGORY	SOURCE MOLAR REACTIVITIES		
	2-GROUP SCHEME	5-GROUP SCHEME	6-GROUP SCHEME
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION			
Petroleum Production and Refining			
Petroleum Production	.16	.19	.12
Petroleum Refining	.89	.71	.71
Gasoline Marketing			
Underground Service Station Tanks	.82	.71	.71
Auto Tank Filling	.96	.78	.79
Fuel Combustion	.10	.20	.18
Waste Burning & Fires	.28	.37	.38
STATIONARY SOURCES-ORGANIC CHEMICALS			
Surface Coating			
Heat Treated	.80	.70	.70
Air Dried	.86	.69	.69
Dry Cleaning			
Petroleum Based Solvent	1.00	.66	.66
Synthetic Solvent (PCE)	.00	.10	.10
Degreasing			
TCE Solvent	1.00	.95	.95
1,1,1-T Solvent	.00	.10	.10
Printing			
Rotogravure	.84	.62	.62
Flexigraphic	.81	.76	.76
Industrial Process Sources			
Rubber & Plastic Manf.	.84	.97	.98
Pharmaceutical Manf.	.66	.64	.64
Miscellaneous Operations	.56	.53	.53
MOBILE SOURCES			
Gasoline Powered Vehicles			
Light Duty Vehicles			
Exhaust Emissions	.72	.72	.72
Evaporative Emissions	.96	.80	.80
Heavy Duty Vehicles			
Exhaust Emissions	.72	.72	.72
Evaporative Emissions	.96	.80	.80
Other Gasoline Powered Equipment			
Exhaust Emissions	.72	.72	.72
Evaporative Emissions	.96	.80	.80
Diesel Powered Motor Vehicles	.87	1.02	1.01
Aircraft			
Jet	.91	.88	.88
Piston	.66	.74	.72
WEIGHTED AVERAGE OF ALL SOURCES	0.70	0.66	0.66

most of the source types. Twenty-one of the 26 major source types have molar reactivities in the range .66 to 1.00 for the 2- group scheme, .62 to 1.02 for the 5-group scheme, and .62 to 1.01 for the 6-group scheme. Only five types of sources have very low molar reactivity: petroleum production, fuel combustion, waste burning & fires, synthetic dry cleaning solvent (PCE), and 1,1,1-T degreasing. Each of these categories have large fractions of emissions in Class I of the reactivity classification scheme.

The reason for the general uniformity is that the emissions from many sources tend to consist largely of compounds in Classes III and IV of the reactivity classification scheme (See Table 3-63). This provides for a general homogeneity of source molar reactivities. The fractions which tend to occur in Classes 0, I and V lead to some deviations in individual source reactivity ratings, but these deviations are not very great (with the five exceptions noted above).

Another significant feature of the source molar reactivity listing is that the reactivities for the 5-group and 6-group schemes are nearly identical. The reader is reminded that the difference between the 5-group and 6-group schemes is that methane is assigned a molar reactivity of .1 in the 5-group scheme but is assigned zero reactivity in the 6-group scheme. Basically, the only sources which are affected by this change are petroleum production, fuel combustion, and waste burning & fires. Methane is a significant portion of the emissions from each of these three source types.

Relative source molar reactivities are significantly different for the 2-group and 5-group schemes. The 5-group rating has been calibrated so that light duty vehicle exhaust (.72) is the same in each scheme. Ratings for other gasoline engines, degreasing solvents, pharmaceutical manufacturing, and miscellaneous chemical manufacturing also remain about the same for each scheme. However, relative reactivity ratings with the 5-group scheme are significantly lower than with the 2-group scheme for sources involving evaporated gasoline, surface coatings, petroleum dry cleaning solvent, and printing solvents. On the other hand, relative reactivity ratings become greater with the 5-group scheme for petroleum production, fuel combustion, waste burning, rubber/plastic manufacturing, diesels, and aircraft.

4.2 SOURCE WEIGHT REACTIVITIES

Source weight reactivities (SWR^k) for the k-group scheme are calculated from source molar reactivities according to the formula,

$$SWR^k = \frac{MW_{ex} \cdot SMR^k}{MW} ,$$

where

SMR^k = the (k-group) source molar reactivity of the source in question,

MW_{ex} = the average molecular weight of auto exhaust,

and MW = the average molecular weight of the source in question. The above formula has been chosen so that auto exhaust will again have a reactivity of .72. All other sources will have source weight reactivities relative to auto exhaust in proportion to reactive moles per unit weight of emissions. It should be noted that source weight reactivity for the 2-group scheme is not the per cent by weight of reactive emissions (See Section 1.1).

Table 4-2 lists the source weight reactivities for each of the 17 types of stationary sources and 9 types of mobile sources considered in this study. Also listed for comparison are the source molar reactivities and the average source molecular weights.

The source weight reactivities show about the same overall uniformity as the source molar reactivities. For instance, the most reactive 21 of the 26 source types have weight reactivities in the range .52 to .98 for the 2-group scheme and .60 to .92 for the 5-group scheme. Similar ranges for source molar reactivities are .66 to 1.00 and .62 to 1.01, respectively.

As with the source molar reactivities, there is little difference between the 5-group and 6-group schemes, with the exception of petroleum production, fuel combustion, and waste burning and fires. Also, there again is a significant change in relative source reactivities between the 2-group and 5-group schemes.

TABLE 4-2. SOURCE WEIGHT REACTIVITIES FOR THE 2-, 5-, AND 6- GROUP SCHEMES

SOURCE CATEGORY	SOURCE MOLAR REACTIVITIES			AVERAGE MOLECULAR WEIGHT	SOURCE WEIGHT REACTIVITIES		
	2-GROUP SCHEME	5-GROUP SCHEME	6-GROUP SCHEME		2-GROUP SCHEME	5-GROUP SCHEME	6-GROUP SCHEME
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION							
Petroleum Production and Refining							
Petroleum Production	.16	.19	.12	29	.38	.45	.29
Petroleum Refining	.89	.71	.71	93	.66	.53	.53
Gasoline Marketing							
Underground Service Station Tanks	.82	.71	.71	58	.98	.84	.84
Auto Tank Filling	.96	.78	.79	74	.90	.73	.74
Fuel Combustion	.10	.20	.12	25	.28	.55	.33
Waste Burning & Fires	.26	.37	.32	33	.54	.77	.67
STATIONARY SOURCES-ORGANIC CHEMICALS							
Surface Coating							
Heat Treated	.80	.70	.70	82	.67	.59	.59
Air Dried	.86	.69	.69	87	.68	.55	.55
Dry Cleaning							
Petroleum Based Solvent	1.00	.66	.66	126	.55	.36	.36
Synthetic Solvent (PCE)	.00	.10	.10	166	.00	.04	.04
Degreasing							
TCE Solvent	1.00	.95	.95	132	.52	.50	.50
1,1,1-T Solvent	.00	.10	.10	134	.00	.05	.05
Printing							
Rotogravure	.84	.62	.62	82	.69	.52	.52
Flexigraphic	.81	.76	.76	57	.98	.92	.92
Industrial Process Sources							
Rubber & Plastic Manf.	.84	.97	.98	73	.79	.92	.93
Pharmaceutical Manf.	66	.64	.64	75	.61	.59	.59
Miscellaneous Operations	.56	.53	.53	80	.48	.46	.46
MOBILE SOURCES							
Gasoline Powered Vehicles							
Light Duty Vehicles							
Exhaust Emissions	.72	.72	.72	69	.72	.72	.72
Evaporative Emissions	.95	.80	.80	91	.72	.61	.61
Heavy Duty Vehicles							
Exhaust Emissions	.72	.72	.72	69	.72	.72	.72
Evaporative Emissions	.95	.80	.80	91	.72	.61	.61
Other Gasoline Powered Equipment							
Exhaust Emissions	.72	.72	.72	69	.72	.72	.72
Evaporative Emissions	.95	.80	.80	91	.72	.61	.61
Diesel Powered Motor Vehicles	.87	1.02	1.01	89	.67	.79	.78
Aircraft							
Jet	.91	.88	.88	121	.52	.50	.50
Piston	.66	.74	.72	56	.81	.91	.89
WEIGHTED AVERAGE OF ALL SOURCES	0.70	0.66	0.66	71.9	0.67	0.64	0.63

The most important feature of Table 4-2 is the difference in relative ratings of various sources for molar vs. weight reactivities. Sources with high average molecular weight are of lesser relative importance for weight reactivity. For instance, TCE degreasing solvent is one of the most reactive source categories according to molar reactivity but is one of the least reactive categories according to weight reactivity. Other sources that have weight reactivities that are notably lower than molar reactivities are petroleum refining, surface coating, dry cleaning, rotogravure printing, evaporative emissions from automobiles, diesels, and jet aircraft. Sources with low average molecular weight become of greater relative importance in terms of weight reactivity. For instance, the relative weight reactivities of petroleum production, fuel combustion, and waste burning & fires are more than twice their molar reactivities. Other sources with low average molecular weights (and higher weight reactivities) are underground service station tanks, flexigraphic printing, and piston aircraft.

4.3 REACTIVE EMISSIONS

Reactive emissions are computed as a product of total weight emissions times source weight reactivity. A molar reactive emission scale directly proportional to the weight reactive emission scale can be calculated by multiplying total molar emissions by source molar reactivity. Table 4-3 presents reactive weight emissions for the 2-, 5-, and 6- group reactivity classification schemes. Also presented are the percentage contributions of each source type to total reactive emissions. Table 4-3a is in English units, while Table 4-3b is in metric units.

Table 4-3 illustrates that the percentage contribution of some sources changes significantly when reactivity factors are added to total organic emissions. For instance, petroleum production constitutes 2.3% of total weight emissions but only 1.4%, 1.7%, and 1.1% of 2-, 5-, and 6- group reactive emissions, respectively. Synthetic dry cleaning solvent (PCE) comprises 1.0% of total organic emissions by weight but only, 0.0%, 0.1%, and 0.1% of reactive emissions for the three reactivity schemes, respectively. 1,1,1-T solvent comprises 3.6% of total organics but only 0.0%, 0.3%, or 0.3% of reactive organics. Rubber and plastic manufacturing accounts for 1.6% of total emissions but 1.9%, 2.3%, or 2.4% of reactive emissions. Underground

TABLE 4-3. REACTIVE EMISSION INVENTORIES FOR THE 2-, 5-, AND 6- GROUP SCHEMES (English Units)

SOURCE CATEGORY	TOTAL EMISSIONS		REACTIVE EMISSIONS					
	TONS/DAY	% OF TOTAL	REACTIVE TONS/DAY*			PERCENT OF TOTAL		
			2-GROUP SCHEME	5-GROUP SCHEME	6-GROUP SCHEME	2-GROUP SCHEME	5-GROUP SCHEME	6-GROUP SCHEME
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION								
Petroleum Production and Refining								
Petroleum Production	62	2.3	24	28	18	1.4	1.7	1.1
Petroleum Refining	50	1.9	33	27	27	1.9	1.6	1.6
Gasoline Marketing								
Underground Service Station Tanks	48	1.8	47	40	40	2.7	2.4	2.4
Auto Tank Filling	104	4.0	94	76	77	5.4	4.6	4.7
Fuel Combustion	23	0.9	6	13	8	0.3	0.8	0.5
Waste Burning & Fires	41	1.6	22	32	27	1.3	1.9	1.6
STATIONARY SOURCES-ORGANIC CHEMICALS								
Surface Coating								
Heat Treated	14	0.5	9	8	8	0.5	0.5	0.5
Air Dried	129	5.0	88	71	71	5.0	4.3	4.3
Dry Cleaning								
Petroleum Based Solvent	16	0.6	9	6	6	0.5	0.4	0.4
Synthetic Solvent (PCE)	25	1.0	0	1	1	0.0	0.1	0.1
Degreasing								
TCE Solvent	11	0.4	6	5	5	0.3	0.3	0.3
1,1,1-T Solvent	95	3.6	0	5	5	0.0	0.3	0.3
Printing								
Rotogravure	31	1.2	21	16	16	1.2	1.0	1.0
Flexigraphic	15	0.6	15	14	14	0.8	0.8	0.8
Industrial Process Sources								
Rubber & Plastic Manf.	42	1.6	33	39	39	1.9	2.3	2.4
Pharmaceutical Manf.	16	0.6	10	9	9	0.6	0.5	0.5
Miscellaneous Operations	83	3.2	40	38	38	2.3	2.5	2.3
MOBILE SOURCES								
Gasoline Powered Vehicles								
Light Duty Vehicles								
Exhaust Emissions	780	30.0	562	562	562	32.1	33.9	34.2
Evaporative Emissions	481	18.5	346	293	293	19.8	17.7	17.9
Heavy Duty Vehicles								
Exhaust Emissions	285	10.9	205	205	205	11.7	12.3	12.5
Evaporative Emissions	67	2.6	48	41	41	2.7	2.5	2.5
Other Gasoline Powered Equipment								
Exhaust Emissions	110	4.2	79	79	79	4.5	4.8	4.8
Evaporative Emissions	22	0.8	16	13	13	0.9	0.8	0.8
Diesel Powered Motor Vehicles	12	0.5	8	9	9	0.5	0.5	0.5
Aircraft								
Jet	20	0.8	10	10	10	0.6	0.6	0.6
Piston	22	0.9	18	20	20	1.0	1.2	1.2
TOTAL	2604	100%	1749	1660	1641	100%	100%	100%

* To convert to reactive ton moles per day, multiply by 0.0145

TABLE 4-3. REACTIVE EMISSION INVENTORIES FOR (continued) THE 2-, 5-, AND 6- GROUP SCHEMES (Metric Units)

SOURCE CATEGORY	TOTAL EMISSIONS		REACTIVE EMISSIONS					
	METRIC TONS/DAY	% OF TOTAL	REACTIVE METRIC TONS/DAY*			PERCENT OF TOTAL		
			2-GROUP SCHEME	5-GROUP SCHEME	6-GROUP SCHEME	2-GROUP SCHEME	5-GROUP SCHEME	6-GROUP SCHEME
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION								
Petroleum Production and Refining								
Petroleum Production	55	2.3	21	25	16	1.4	1.7	1.1
Petroleum Refining	45	1.9	30	24	24	1.9	1.6	1.6
Gasoline Marketing								
Underground Service Station Tanks	44	1.8	43	36	36	2.7	2.4	2.4
Auto Tank Filling	94	4.0	85	69	70	5.4	4.6	4.7
Fuel Combustion	21	0.9	5	12	7	0.3	0.8	0.5
Waste Burning & Fires	37	1.6	20	29	24	1.3	1.9	1.6
STATIONARY SOURCES-ORGANIC CHEMICALS								
Surface Coating								
Heat Treated	13	0.5	8	7	7	0.5	0.5	0.5
Air Dried	117	5.0	80	64	64	6.0	4.3	4.3
Dry Cleaning								
Petroleum Based Solvent	15	0.6	8	5	5	0.5	0.4	0.4
Synthetic Solvent (PCE)	23	1.0	0	1	1	0.0	0.1	0.1
Degreasing								
TCE Solvent	10	0.4	5	5	5	0.3	0.3	0.3
1,1,1-T Solvent	86	3.6	0	4	4	0.0	0.3	0.3
Printing								
Rotogravure	28	1.2	19	15	15	1.2	1.0	1.0
Flexigraphic	14	0.6	14	13	13	0.9	0.8	0.9
Industrial Process Sources								
Rubber & Plastic Manf.	38	1.6	30	35	35	1.9	2.3	2.4
Pharmaceutical Manf.	15	0.6	9	8	8	0.6	0.5	0.5
Miscellaneous Operations	75	3.2	36	34	34	2.3	2.3	2.3
MOBILE SOURCES								
Gasoline Powered Vehicles								
Light Duty Vehicles								
Exhaust Emissions	707	30.0	510	510	510	32.1	33.9	34.2
Evaporative Emissions	436	18.5	314	266	266	19.8	17.7	17.9
Heavy Duty VEhicles								
Exhaust Emissions	258	10.9	186	186	186	11.7	12.3	12.5
Evaporative Emissions	61	2.6	44	37	37	2.7	2.5	2.5
Other Gasoline Powered Equipment								
Exhaust Emissions	100	4.2	72	72	72	4.5	4.8	4.8
Evaporative Emissions	20	0.8	15	12	12	0.9	0.8	0.8
Diesel Powered Motor Vehicles	11	0.5	7	9	9	0.5	0.5	0.5
Aircraft								
Jet	18	0.8	9	9	9	0.6	0.6	0.6
Piston	20	0.9	16	18	18	1.0	1.2	1.2
TOTAL	2362	100%	1586	1505	1487	100%	100%	100%

* To convert to reactive metric ton moles per day, multiply by 0.0145

service station tanks constitute 1.8% of total emissions but 2.7%, 2.4% or 2.4% of reactive emissions.

The relative contribution of exhaust emissions from gasoline engines is not significantly affected by using reactivity criteria. The contribution from exhaust of all gasoline engines (LDV's, HDV's, and other equipment) is 45.1% of the total organic inventory. Using the 2-, 5-, and 6- group schemes, the contribution to reactive organics is 48.3%, 51.0% and 51.5% respectively.

Likewise, the relative contribution of evaporative emissions from gasoline engines (LDV's, HDV's, and other equipment) is not significantly altered. These emissions contribute 21.9% to the total organic inventory and 23.4%, 21.0% & 21.2% to reactive inventories based on the 2-, 5-, & 6- group schemes, respectively.

All in all, the impact of using various reactivity criteria to compute relative source contributions is certainly less than dramatic. Generally, the total organic inventory is quite similar to each of the three reactive inventories. The only notable differences occur among minor source types. The overall similarity between the nonreactive and reactive inventories may be a preliminary indication that a general policy of indiscriminate control (with special considerations for only a few sources) is an appropriate strategy for organics. However, it is premature to adopt this conclusion. Chapter 6 will perform more in-depth analyses in order to determine the costs and benefits involved in applying reactivity criteria to organic control policy.

5.0 EMISSION REDUCTION STRATEGIES FOR ORGANIC SOURCES

The previous chapter derived reactivity ratings for organic emission sources in the Metropolitan Los Angeles AQCR. These reactivity ratings are important to organic control policy because they allow a selective approach to be taken in formulating emission reduction strategies. The present chapter determines source emission reductions based on reactivity criteria and compares these results to strategies based on indiscriminate control of organics.

This chapter is organized in three sections. Section 5.1 discusses the overall degree of reactive organic control that is required to attain the national air quality standard for oxidant in the Los Angeles region. It is found that substantial uncertainty surrounds present estimates for degree of control required and that even 100% control of man-made sources may not be sufficient to attain the oxidant air quality standard. An overall reduction of reactive organics by 90% is selected as an arbitrary target level for the purposes of this study. Section 5.2 describes guidelines for determining individual source emission reductions which attain a given overall degree of control. These guidelines include economic efficiency principles as well as criteria which can be used when economic data are unavailable. Section 5.3 determines emission reductions for individual organic source categories for the Metropolitan Los Angeles AQCR. The emission reductions are determined both for indiscriminate control and control based on reactivity ratings.

5.1 OVERALL DEGREE OF REACTIVE HYDROCARBON CONTROL REQUIRED FOR LOS ANGELES

Considerable uncertainty surrounds the relationship between ambient oxidant levels and precursor emission levels. This uncertainty has resulted in an ongoing controversy concerning the percentage reduction in reactive organic emissions that would be necessary to achieve the national ambient air quality standard for oxidant in the Los Angeles region. On one hand, it can be argued that background sources of reactive hydrocarbons are sufficiently large to produce violations of the oxidant standard in Los Angeles even if all man-made hydrocarbon sources were completely eliminated. At the opposite extreme, it has been contended that the present new car control program may attain the oxidant air quality standard in Los Angeles in the early 1980's [1], even though the associated reduction in total regionwide organic emissions will be only about 60% from 1972 levels.

In this study, it will not be possible to resolve the issue concerning the degree of reactive organic emission reduction required for Los Angeles. However, to put some light on the issue, the problem will be reviewed below using the results of several recent oxidant air quality analyses. This review will indicate that the overall reactive organic reduction for Los Angeles should be at least 85% and probably as high as 95%.

There are several factors leading to uncertainty concerning the overall reduction in reactive organic emissions that is required to attain the oxidant standard. A principal factor is the lack of a reliable modelling methodology for relating oxidant concentrations to HC and NO_x precursors. Three general modelling approaches have been followed: smog chamber simulation, statistical/empirical analysis of aerometric data, and mathematical physicochemical modelling. Presently, each approach involves very significant limitations. Here, the results of several empirical and smog chamber models will be reviewed to summarize existing evidence pertaining to the degree of reactive organic control needed for Los Angeles.

A second important area of uncertainty involves background levels, both for hydrocarbons and for ozone. A very recent study indicates that about 12 to 13%* by weight of nonmethane organics in the Los Angeles atmosphere are from "geogenic" sources, [2]. The existence of this background level limits the oxidant reductions that can be achieved by controlling the source categories listed in the man-made emission inventory. Existing air quality models do not account for the background organic level.

Present air quality models also neglect background ozone contributions. Natural background ozone apparently occurs in the range of .01 to .06 PPM [3], a significant level compared to the .08 PPM air quality standard. However, neglecting background ozone in modelling the Los Angeles urban atmosphere is probably not important since NO emissions in Los Angeles tend to suppress ozone levels to nearly zero during the night. Before the photochemical reactions begin in the morning, ozone concentrations in Los Angeles are typically less than .01 PPM. In reviewing the modelling studies below, background hydrocarbon and ozone contributions will be neglected.

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* The results of reference [2] have been modified slightly by including organic solvent and other miscellaneous contributions which were neglected in that study.

A third area of uncertainty in calculating required reactive organic reductions involves the role of NO_x. Ambient oxidant levels depend on emission levels of both organics and nitrogen oxides. The degree of organic emission reductions that is necessary to achieve the oxidant standard will depend on the level of NO_x emissions. In the analysis below, it will be assumed that NO_x concentrations will remain at 1972 levels. This assumption appears reasonable in light of recent emission projections for Los Angeles which indicate that the reductions in NO_x from motor vehicles will be nearly cancelled by increases in NO_x from other sources during the 1970's, [4].

A final area of uncertainty involves oxidant measurement techniques. It has been found that Los Angeles County APCD procedures yield oxidant values that frequently differ substantially from measurements made with EPA procedures,[5]. Some of the empirical models reviewed below use data taken with the EPA procedure, while others use Los Angeles APCD data. The results of the various empirical models should be standardized to a single monitoring method. Since sufficient information to perform a rigorous standardization is not available, the models will be used here in their original form. Accordingly, the discrepancies in the aerometric data base should be noted as a potential source of error in the analysis presented below.

5.1.1 Review of Oxidant/Precursor Models

This section reviews the results of six oxidant/precursor methodologies which have been applied to the Los Angeles region. The first four models involve empirical analyses of aerometric data; the last two models are based on smog chamber simulation. Each model is reviewed specifically with respect to the overall degree of reactive organic control that is indicated for attaining the oxidant standard in the Los Angeles region. As noted above, it will be assumed that total NO_x emissions remain fixed at the 1972 level in calculating required reactive organic reductions.

EPA Los Angeles Aerometric Model

Schuck and Papetti [6], used the "upper limit" approach to analyze the relationship between maximal one hour oxidant and hydrocarbons. They produced two types of upper limit curves for the Los Angeles region. The first type, illustrated in Figure 5-1, is equivalent to the EPA Appendix J approach, [7], [8]. For each of the three locations listed in Figure 5-1, the solid line represents the upper limit of daily maximum one hour oxidant values that are associated with various concentrations of 6-9 a.m. nonmethane hydrocarbons.* The daily maximum oxidant levels and the early morning hydrocarbon levels represent data taken at the same location from 1968 to 1971. The dashed lines in Figure 5-1 are extrapolations of the upper limit curves to zero based on data from other large U.S. cities which experience lower hydrocarbon concentrations than Los Angeles.

Figure 5-2 illustrates the second type of upper limit curve derived for the Los Angeles region. This curve gives the upper limit of daily maximal oxidant levels measured anywhere in the basin for various values of 6-9 a.m. nonmethane hydrocarbons averaged over 8 stations in the basin. This figure is based on 1971 data only.

Using Figures 5-1 and 5-2, Schuck and Papetti calculated the overall degree of reactive hydrocarbon control needed to attain the .08 PPM oxidant standard in the Los Angeles region. Figure 5-1 indicated that 93% control was required from the 1971 emission level. Figure 5-2 implied 91% control from the 1971 level. These levels of control were calculated by noting the maximal oxidant level in 1971 (point A in Figure 5-2), finding the associated maximal NMHC level (point A'), and then determining the degree of control (to point B') required to attain the ambient standard (point B). Allowing for emission reductions which occurred between 1971 and 1972, the corresponding degrees of control from 1972 emission levels would still be approximately 93% and 91% respectively.

To put the results of the EPA upper limit model in perspective, it is useful to note some of the sources of error in the analysis. The following list summarizes the main limitations:

- The upper limit model is subject to inaccuracies in the aerometric data base for oxidant and total hydrocarbons. Calculating NMHC levels from total hydrocarbon levels introduces another source of error.

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*Nonmethane hydrocarbons were not actually measured as such. Rather, nonmethane hydrocarbons were computed from total hydrocarbon measurements according to the formula,

$$NMHC = .7 (THC-1.3).$$

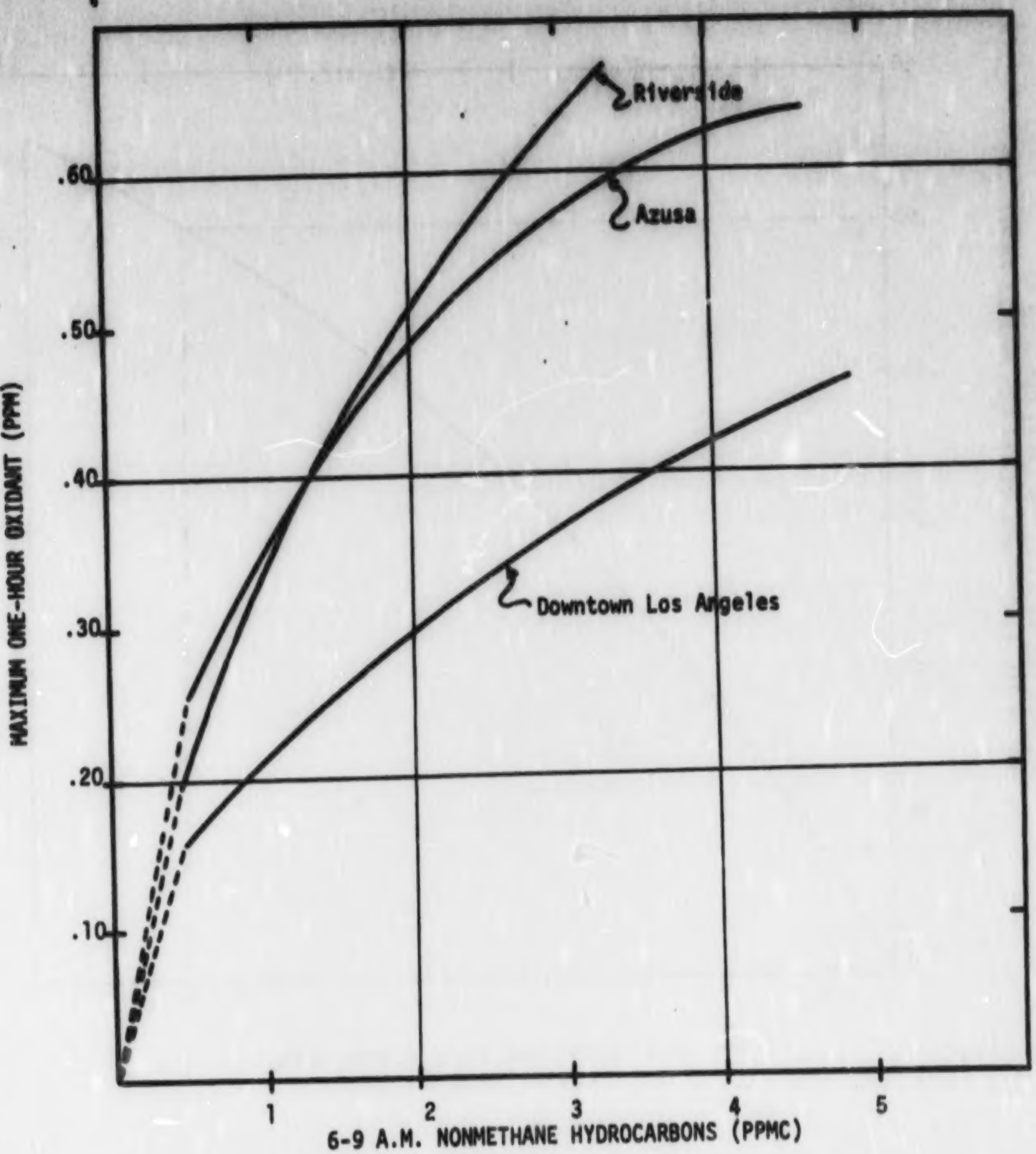

Figure 5-1. Upper Limit Curves for Three Stations in the Metropolitan Los Angeles AQCR, [6]

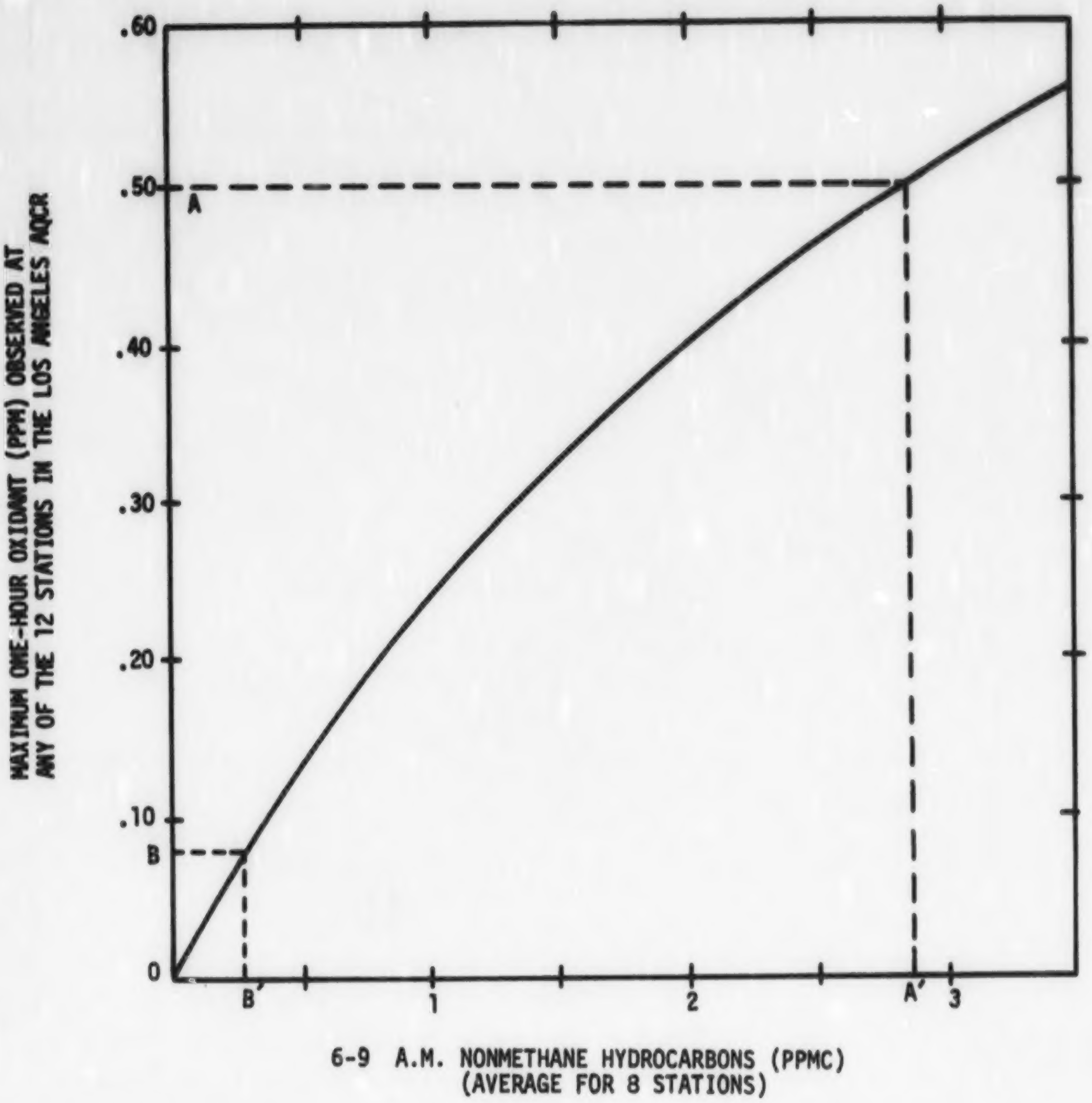

Figure 5-2 Aggregated Upper Limit Curve for the Metropolitan Los Angeles AQCR, [6].

- The role of NO_x in oxidant formation is neglected. The present upper limit curves may no longer be appropriate if the HC/NO_x emission ratio is altered.

- Relating oxidant concentrations to 6:00-9:00 A.M precursor concentrations neglects the role of post 9:00 A.M. emissions im oxidant production.

- The EPA Appendix J approach (Figure 5-1) does not account for transport. Early morning precursor and afternoon oxidant measurements at one location are likely associated with two different air masses. The modified approach (Figure 5-2) does account for transport, but only in an approximate, aggregated way.

- The effect of meteorological variables is not accounted for. The observed relationship of max oxidant to hydrocarbons may be spurious in the sense that it may be due to a mutual correlation with unaccounted for meteorological variables.

- The upper limit curves are not defined in a statistically meaningful manner. Likewise, the calculation of degree of control required neglects statistical considerations.

Chevron Research Company Aerometric Model

Merz, Painter, and Ryason [9] used regression analysis to examine the relationship between oxidant and early morning precursor levels at downtown Los Angeles. They regressed max daily one hair oxidant against 6 to 9 a.m. concentrations of NO_x and THC. To minimize meteorological variations, and therefore to minimize spurious oxidant/precursor dependencies due to mutual interrelations with metorological variables, data were entered only for the months of Auggst, September, and October.

Using log-linear regression on three months of data for eight years (1962-1969), they obtained the result,

$$\ln OX = 2.6 + .150 \ln \frac{NO_x}{17.5} + .542 \ln \frac{THC}{4.6} , \qquad (5\text{-}1)$$

where [OX] = pphm, $[NO_x]$ = pphm, and [THC] = ppmC.* Making the simple assumption that 50 percent of THC is non-methane HC, they concluded that

$$\ln OX = 2.98 + .150 \ln \frac{NO_x}{17.5} + .542 \ln \frac{NMHC}{4.6} . \qquad (5\text{-}2)$$

This equation served as a basis for the "smog diagram" illustrated in Figure 5-3.

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* The numerical constants, 17.5 and 4.6, are the geometric average values for NO_x and THC.

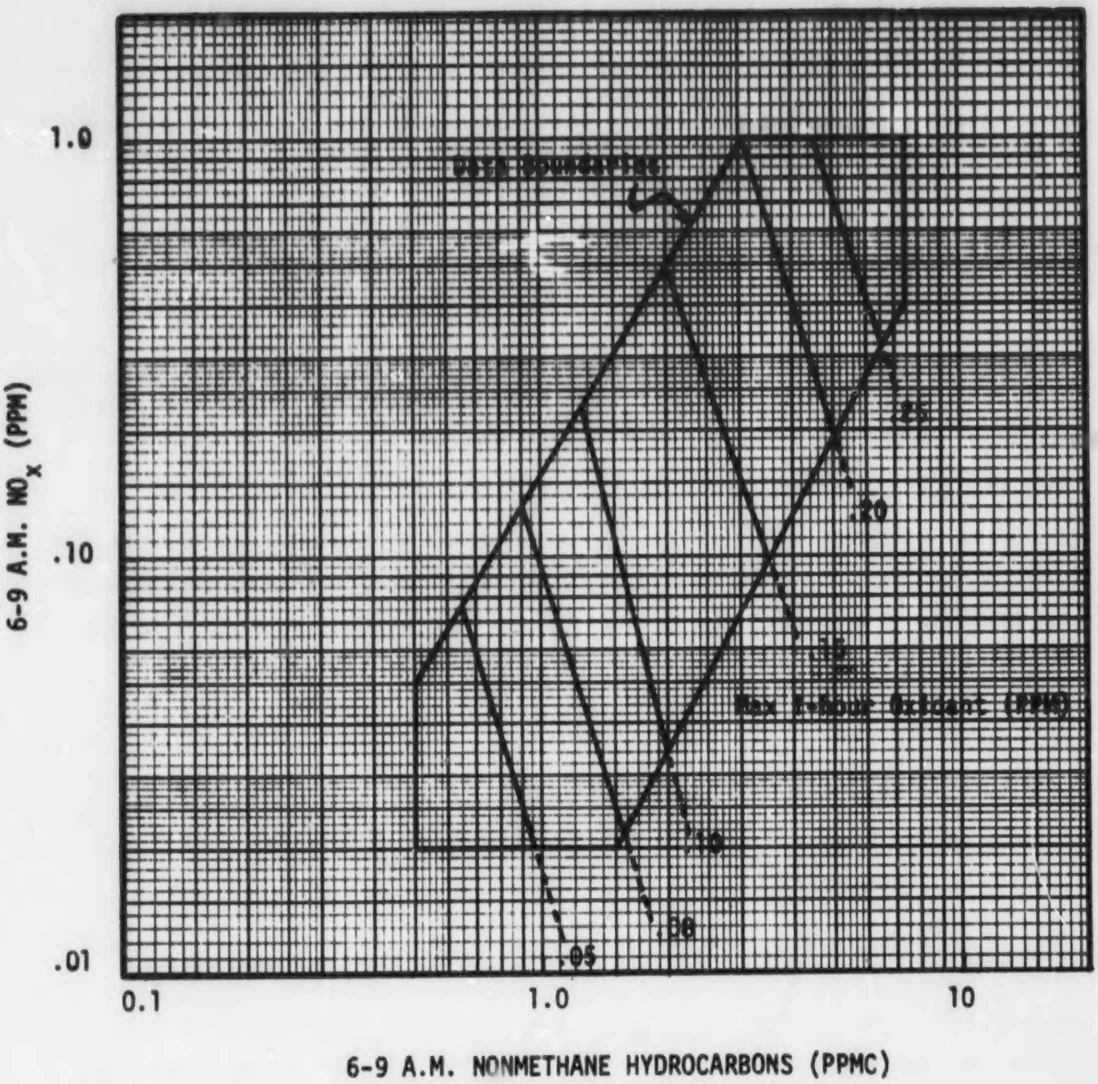

Figure 5-3. Chevron Research Smog Diagram for August-October in Downtown Los Angeles, [9]

Using the smog diagram and a statistical analysis of pollutant concentrations, the Chevron group calculated the degree of NMHC control that would be required to reduce violations of the 10 pphm California oxidant standard to less than 9 hours per year (.1% of all hours) in downtown Los Angeles. They concluded that, for fixed NO_x emissions, NMHC emissions would need to be reduced by 93% from the levels of the late 1960's. From 1972 NMHC emission levels, which are lower than levels of the late sixties, the corresponding degree of control would be 91%.

To reduce violations of the federal oxidant standard (8 pphm) to one hour per year at all locations in the Metropolitan Los Angeles AQCR would require significantly greater hydrocarbon emission control than the case investigated by the Chevron group. As a first guess, one would expect that 91% degree of control for the Chevron case would imply at least 95% control for the more stringent case of attaining the federal standard in the entire air basin.

It is interesting to note that the simple log-linear regression used by Merz, Painter, and Ryason indicated that NO_x reductions would have a slight but beneficial impact on oxidant air quality. This is in contrast to the results of the three models which follow in this discussion. These three models, two based on aerometric data and one on smog chamber data, indicate that NO_x emission reductions would probably have an adverse effect on oxidant air quality.

With three exceptions, the Chevron study involves the same limitations as the Schuck and Papetti analysis or the EPA Appendix J analysis. These exceptions are as follows:

- The Chevron study does include NO_x as well as HC.
- The Chevron analysis minimizes meteorological interferences in the oxidant/precursor relation by restricting input data to three months of the year.
- In the Chevron study, the required degree of control is determined in a more statistically meaningful manner.

California Air Resources Board Aerometric Analysis

Kinosian and Paskind [10] examined the relationship between oxidant and precursors at four locations in the Metropolitan Los Angeles AQCR. They used ambient data for 6-9 A.M. THC and NO_x concentrations and for max-hourly oxidant concentrations measured at the same station. The data base consisted of measurements for July through September from 1969 to 1972. THC measurements were converted to NMHC estimates using correlations established between THC and NMHC at two Los Angeles monitoring sites.

At each location, the data were grouped according to various early morning HC concentrations. For each HC level, a regression was run between oxidant levels and NO_x concentrations. The resulting curves, giving expected oxidant levels as functions of early morning HC and NO_x concentrations, are illustrated in Figure 5-4.

The results of Figure 5-4 cannot be used in a straightforward manner to calculate the overall degree of hydrocarbon control required for the Los Angeles Region. The curves in Figure 5-4 refer to expected max one-hour oxidant during the summer months and not the oxidant level that would occur (for given NMHC and NO_x concentrations) under worst case meteorology (e.g. intense sunlight, persistent inversion, etc.). However, the results of Kinosian and Paskind can be used to obtain some insight into the level of early morning NMHC required for standard attainment. The curves indicate that, at a high oxidant such as Asuza, oxidant levels up to .15 PPM can be produced by 6-9 A.M. NMHC levels of .3 PPMC. Even taking an optimistic approach and assuming that max oxidant is proportionally related to NMHC below .3 PPMC,* the Asuza results imply that NMHC levels of .16 PPMC or lower would be required to attain the federal standard at that site.

Maximal 6-9 A.M. NMHC levels at Asuza were about 4 PPMC in 1972, [10], [11]. A reduction to .16 PPMC would therefore be equivalent to 96% overall degree of control from the 1972 level. This percentage reduction figure may be conservative since a constant NO_x emission level could imply that the HC/NO_x ratio for greatest oxidant formation will no longer occur in the atmosphere (i.e. for very low NMHC levels, morning NO_x levels may be all to the right of the peak of the curves in Figure 5-4). However, counterbalancing that argument, 96% reduction may be too low since the Kimosian and Paskind curves are not for worst case meteorology.

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* This is optimistic since the curves indicate that max oxidant reductions are distinctly less than proportional to NMHC reductions for all the data above .3 PPMC NMHC concentration.

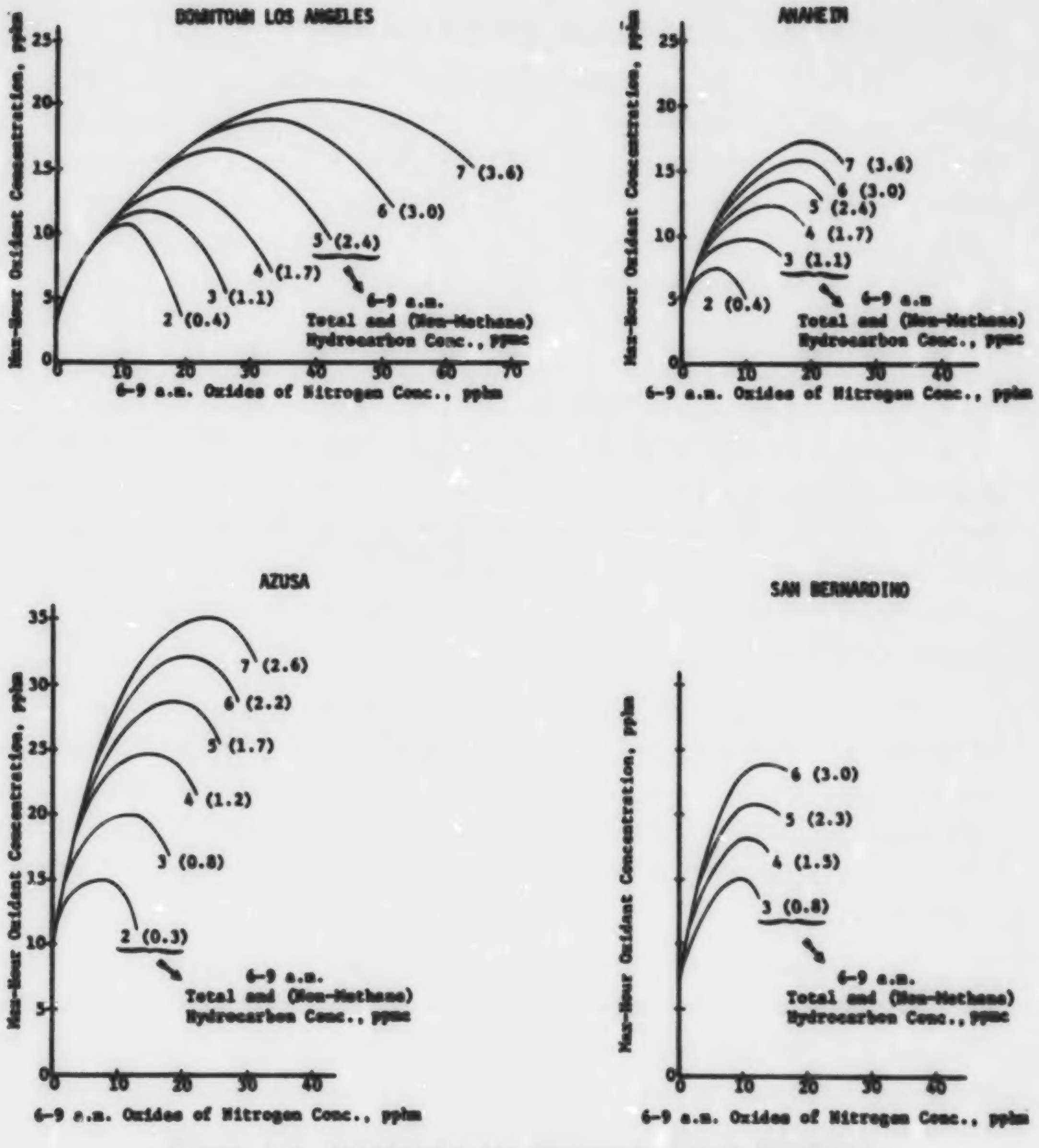

Figure 5-4. California Air Resources Board Aerometric Results, Relationship Between 6-9 A.M. NO_x, 6-9 A.M HC, and Max-Hour Oxidant Concentrations at Selected Sites, [10]

The limitations in using the Kinosian and Paskind results to calculate overall degree of NMHC control are similar to those associated with the Shuck and Papetti analysis. The reader is referred to the previous listing of those limitations.

Environmental Quality Laboratory Aerometric Model

Trijonis [12] used a stochastic model to examine the relationship of oxidant levels in central Los Angeles to hydrocarbon and nitrogen oxide emission levels. For given HC and NO_x emission levels, he determined the joint distribution of morning HC* and NO_x concentrations (7:30-9:30 averages) at downtown Los Angeles from five years of Los Angeles APCD monitoring data (1966-1970). He also determined the probability that mid-day oxidant would violate the state standard (.10 PPM for one hour) as a function of the morning concentrations. For oxidant, an average was taken of maximum one-hour values between 11:00 A.M. and 1:00 P.M. at downtown Los Angeles, Pasadena, and Burbank, weighted according to wind speed and direction, so that the maximum oxidant would correspond as closely as possible to that in the air mass that had been over downtown in the morning. The joint morning HC/NO_x distribution and the probability of a standard violation as a function of morning precursor levels were determined separately for summer and winter.

By assuming that the joint HC/NO_x distribution responds linearly to emissions and that the oxidant standard violation function remains constant as emissions levels change, Trijonis calculated the expected number of days per year that mid-day oxidant in central Los Angeles would exceed the state standard as a function of HC and NO_x emission levels. Figure 5-5 summarizes the results.

The Environmental Quality Lab aerometric model implies that (for fixed NO_x emissions) a 90% reduction in reactive hydrocarbon emissions from the 1972 level is necessary to attain the California oxidant standard (.10 PPM for 1 hour) mid-day in the central Los Angeles area. To meet the more stringent federal oxidant standard (.08 PPM for 1 hour) at all times of the day and throughout the entire AQCR should require a significantly

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* The HC measurements were adjusted for natural background methane using the empirical formula derived by EPA for Los Angeles.

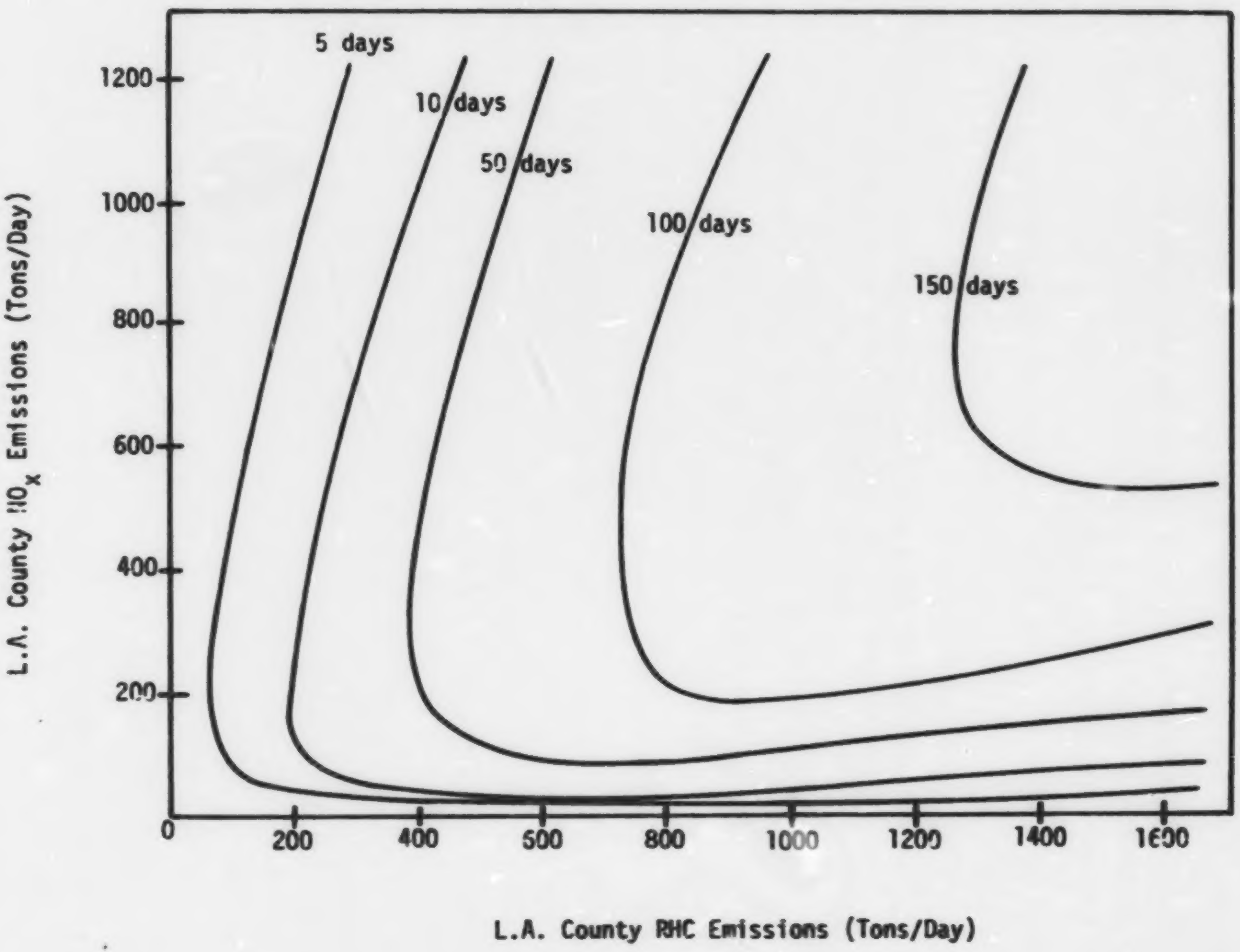

Figure 5-5 Oxidant Air Quality vs. Emissions for Central Los Angeles, [12]

Expected Number of Days Per Year Exceeding .10 ppm vs. NO$_x$ and RHC Emission Levels greater degree of control. As a first guess, at least 95% reactive hydrocarbon control would appear to be necessary to attain the federal standard throughout the basin.

The EQL oxidant model involves many of the same limitations as the other aerometric analyses, (see discussion of Schuck and Papetti model). However, there are several improvements:

- The role of NO_x (as well as hydrocarbons) is explicitly examined.
- Transport is accounted for.
- Interferences in the oxidant/precursor relation from intercorrelations with meteorological variables are reduced by split analyses for summer and winter.
- The results are stated in a statistically well defined manner.

The price of these improvements is that the application was restricted to only mid-day ozone in central Los Angeles.

EPA Smog Chamber Model

Dimitriades [13], [14] investigated the relationship of oxidant to precursors using the results of laboratory smog chamber experiments conducted with auto exhaust. Figure 5-6 summarizes his analysis of emission reduction requirements for attaining the NAAQS for oxidant and nitrogen dioxide. HC and NO_x concentrations in the shaded regions (to the left of line ab or below line bc) yield less than .08 PPM oxidant after six hours of irradiation equivalent to Los Angeles sunlight. NO_x concentrations below line df imply attainment of the national NO_2 standard (.05 PPM, annual average). Point g in the Figure represents the maximal yearly one hour levels of HC and NO_x measured in Los Angeles during the early 1970's, [11].*

A cursory examination of Figure 5-6 would lead to the following conclusions concerning the degree of control required for standard attainment:

- For present NO_x levels, the OX standard could be attained at point h, equivalent to a 65% HC reduction from levels of the early 1970's.
- Both the OX and NO_2 standards could be attained at point e, equivalent to a 90% HC and 74% NO_x reduction from levels of the early 1970's.

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* In Dimitriades' original paper, [13], point g was given at typical concentrations measured in the Los Angeles region rather than yearly maximal one-hour concentrations.

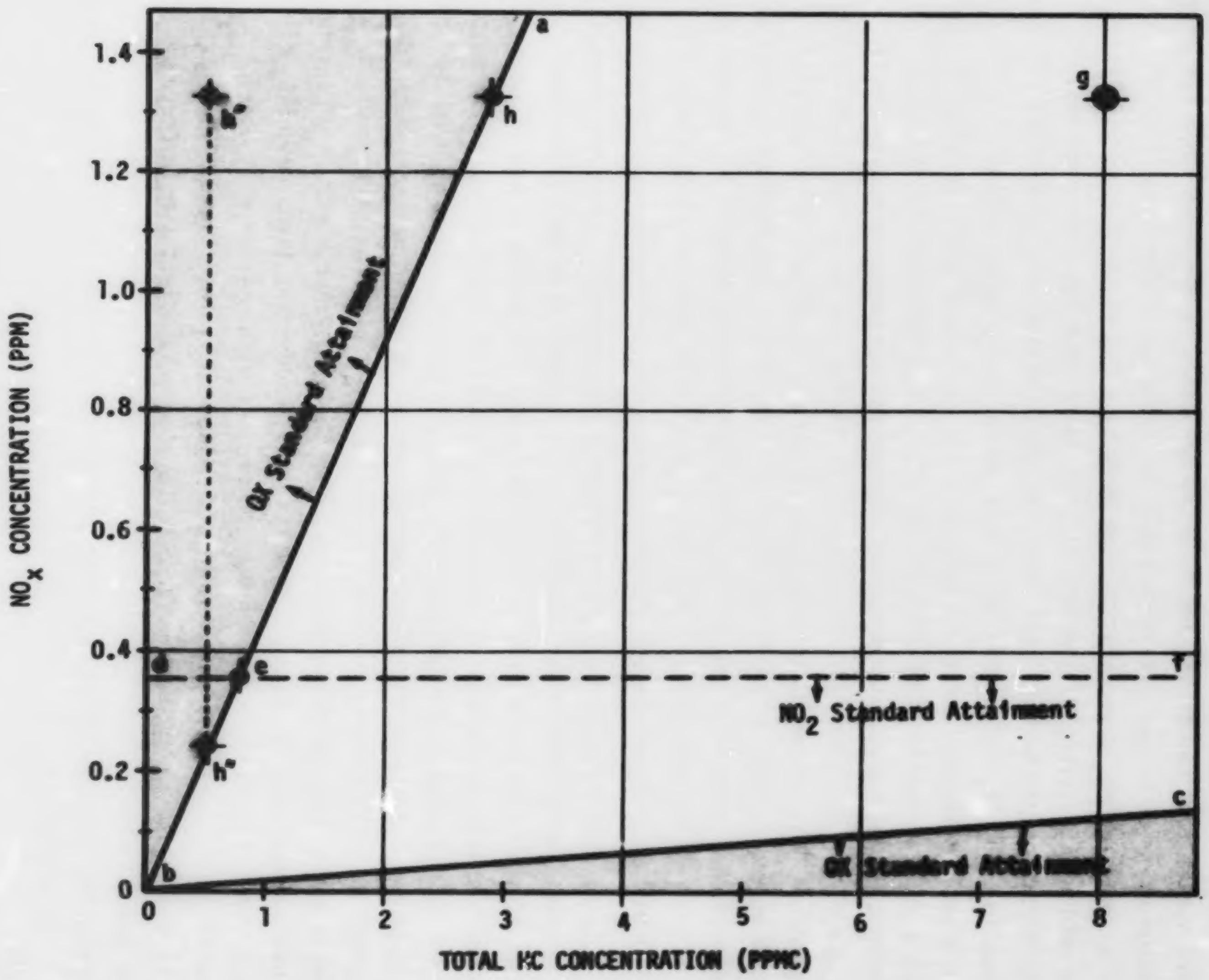

Figure 5-6 EPA Smog Chamber Analysis of Requirements for Attaining the NAAQS for OX and NO$_2$, [13], [14].

However, as Dimitriades points out, the above argument misses a subtle, but very important point, [14]. The ratio of NO_x to HC in the ambient atmosphere varies from day to day and is often considerably different than the average emission ratio, (see Figure 5-7 for example).* For a constant HC value, measured NO_x concentrations can vary by a factor of 5 or more. Thus, the ambient NO_x concentration that is associated with the yearly maximal HC concentrations may be much less than the yearly maximal NO_x concentration. Since lowering NO_x (at either point h or point e) increases oxidant in Dimitriades' diagram, the fluctuations in the ambient HC and NO_x ratio imply that a greater degree of HC control is needed than would be the case if a constant HC/NO_x ratio existed in the atmosphere. Assuming that, on the day of maximal HC concentration, the NO_x concentration can be as few as one fifth the maximal NO_x concentration, the overall degree of HC control required would be represented by point h' rather than point h. For maximal HC concentrations, NO_x concentrations could range anywhere from h" to h'. The degree of HC control for OX standard attainment implied by this argument would be 94% from levels of the early 1970's.

As was the case with aerometric models, smog chamber models are subject to several limitations. The laboratory smog chamber is a very simplified model of the complex processes that occur in the atmosphere. Smog chambers do not simulate the effect of continuous addition of fresh precursor emissions as the day proceeds. Laboratory experiments do not include carry-over effects from previous day smog reactions and may not be of sufficient time duration to represent atmospheric reactions occurring for periods up to 10 hours on a single day. Smog chambers do not simulate the simultaneous effect of several dynamic meteorological process that occur on smoggy days in Los Angeles (e.g. turbulent diffusion, transport to regions with greater mixing height, diurnal solar radiation pattern, etc.). Also, the interactions of pollutants with the ground may be much different than the wall effects which occur in the smog chamber. Finally, auto exhaust or other laboratory test hydrocarbons may not adequately approximate the reactive hydrocarbon mixtures found in real atmospheres.

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* The fluctuations in measured HC/NO_x ratio are not completely understood. Some of the fluctuation may be due to variance in the stationary source areas (HC intensive vs. NO_x intensive areas) that the air mass has encountered. Some may be due to the dependence of evaporative emissions on temperature. Some of the fluctuation may result from a dependence of the HC/NO_x ratio in auto exhaust on ambient temperature and relative humidity.

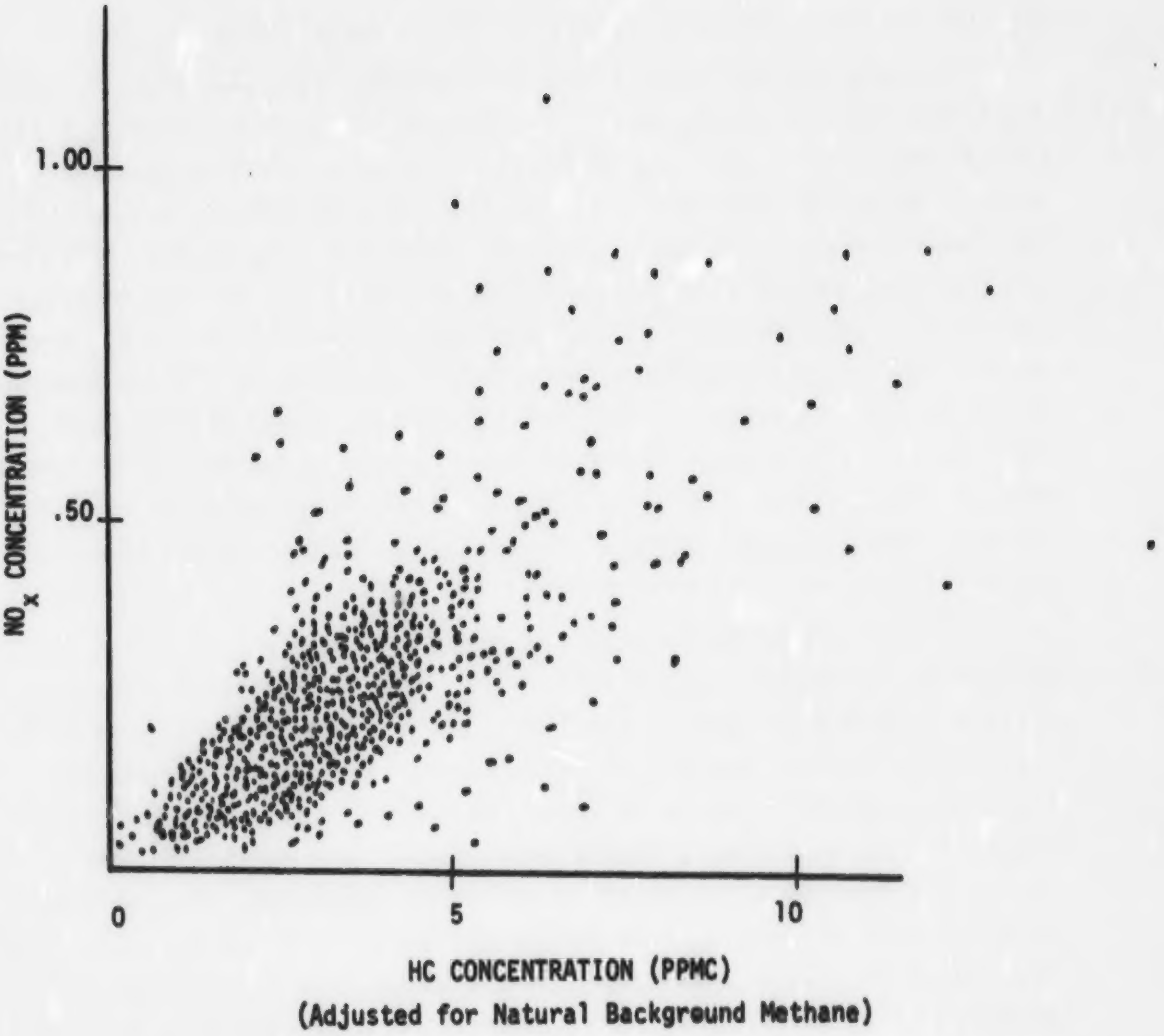

Figure 5-7. Distribution of Morning Precursor Concentrations in Downtown Los Angeles, [4] (7:30 - 9:30 averages)

APCD Smog Chamber Model

Hamming, Chass, Dickinson, and MacBeth [1] of the Los Angeles County APCD used smog chamber tests with auto exhaust to examine the relationship between oxidant and precursors. Figure 5-8 presents the relationship they found between max one hour oxidant (after five hours irradiation) and initial HC and NO_x levels. Point a in Figure 5-8 represents the maximal HC and NO_x concentrations found in Los Angeles in the early 1970's.

A cursory examination of Figure 5-8 indicates that the NAAQS for oxidant can be met (at present NO_x levels) by reducing HC levels to point b, a 73% overall degree of HC control. However, the above argument assumes that maximal ambient HC concentrations will be associated with maximal ambient NO_x concentrations. As noted previously (under the discussion of Dimitriades' results), the ambient HC/NO_x ratio varies substantially from day to day, and the NO_x concentration that is associated with yearly maximal HC levels may be much less than the yearly maximal NO_x concentration. Since lowering NO_x at point b increases oxidant, the fluctuations in the ambient HC/NO_x ratio imply that a greater degree of HC control is needed than that associated with point b. Allowing for this effect, the necessary degree of control becomes point c, 92% HC control. For maximal HC concentrations at point c, NO_x concentrations could range anywhere from c to d.

The above conclusion (that 92% HC control is required to attain the OX standard in the Los Angeles region) should be contrasted with the conclusion reached by Hamming et. al. from Figure 5-8. The Los Angeles APCD staff indicated that the present California new car control program for light-duty vehicles alone would attain the oxidant standard in the Los Angeles region in the early 1980's, even though the reduction in total region wide reactive HC emissions would be only about 60%. The analysis by Hamming et. al. differs from the present analysis in two respects. First, the APCD staff assumed that maximal yearly HC concentrations would be associated with maximal yearly NO_x concentrations. Accordingly, they would contend that the line cd should be represented only by point c. Second, the APCD assumed that only light-duty vehicle emissions would participate in the formation of maximal smog levels. They argue that downtown Los Angeles, where maximal precursor levels are experienced, is subjected to negligible influence from sources other than light-duty vehicles and that

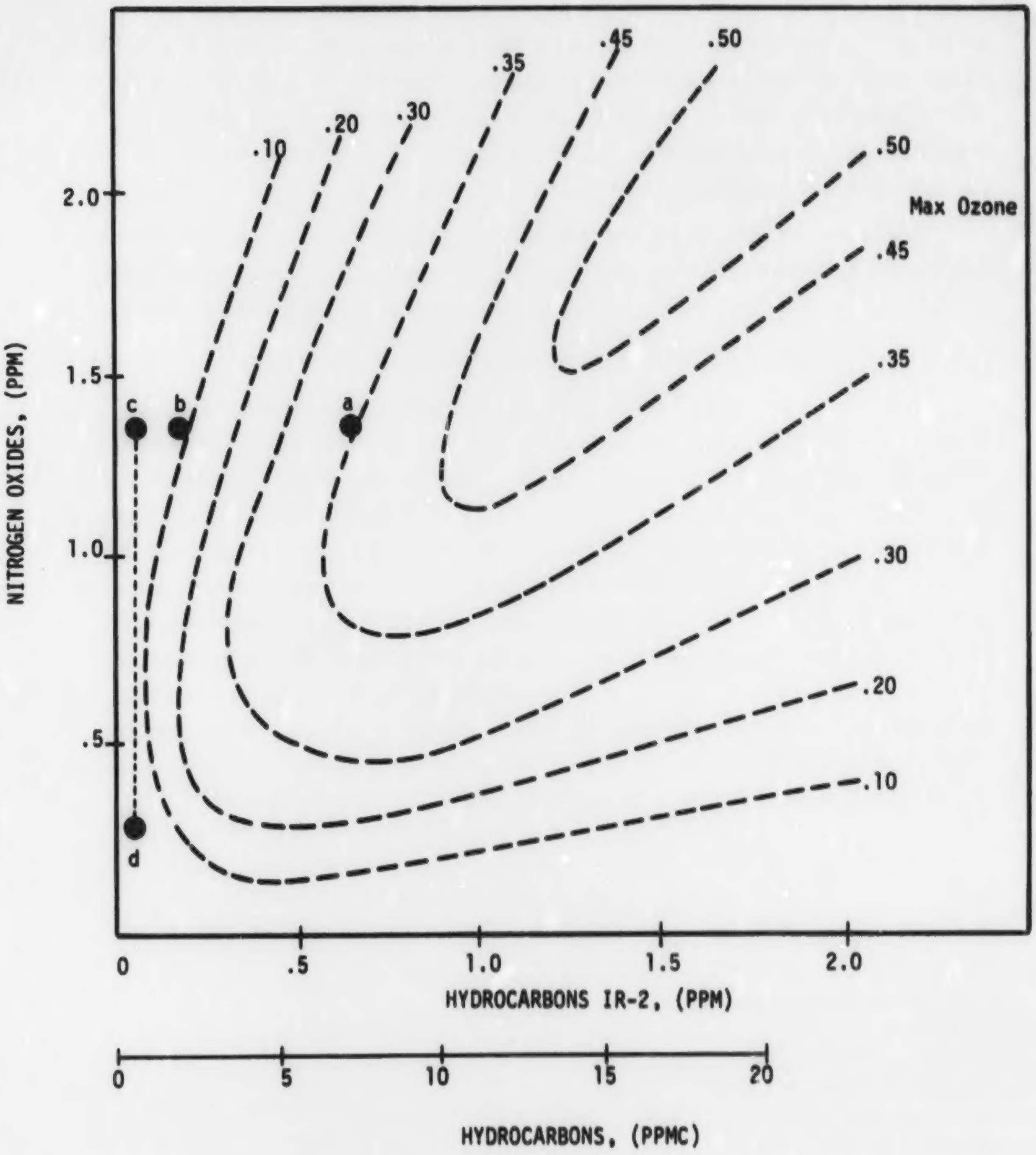

Figure 5-8. Los Angeles APCD Diagram of Max Ozone Concentrations vs. Precursor Concentrations, [1]

no growth in vehicle use will occur in the downtown area. Although total HC emissions in the metropolitan Los Angeles AQCR will be reduced by only 60% in the early 1980's, the APCD calculates that light-duty vehicle HC emissions (with no growth in miles travelled) will be reduced by 87% in the downtown Los Angeles area from the early 1970's to the early 1980's.

As noted earlier, there are important limitations in using smog chamber results to determine control requirements for real atmospheres. The reader is referred to the discussion of these limitations in the previous section.

5.1.2 Conclusions with Respect to Required Emission Reductions

Table 5-1 summarizes the conclusions reached by the examination of alternative oxidant/precursor models in the previous section. The degree of RHC control required (according to our interpretation of each model) is listed for the six models. The estimates of required RHC control obtained from the alternative models are notably similar; the values range from 91% to greater than 95%. The apparent agreement among the models should be viewed with some caution. First, all models were subject to our interpretation which may differ from other interpretations. For instance, we assumed that maximal atmospheric HC levels could be associated with a wide range of NO_x levels rather than with maximal NO_x levels alone. Variance in the ambient

TABLE 5-1. ESTIMATES OF REQUIRED DEGREE OF RHC CONTROL FOR OX STANDARD ATTAINMENT IN THE METROPOLITAN LOS ANGELES AQCR *

Model	TRW's Interpretation of Degree of RHC Control Implied by the Model
EPA Los Angeles Aerometric Model [6]	91-93%
Chevron Research Company Aerometric Model [9]	> 95%
California Air Resources Board Aerometric Analysis [10]	96%
Environmental Quality Laboratory Aerometric Model [12]	> 95%
EPA Smog Chamber Model [13]	94%
LA County APCD Smog Chamber Model [1]	92%

*In calculating the required degree of RHC control, NO_x emissions were assumed to remain constant at the 1972 emission levels.

HC/NO_x ratio (for fixed emission levels) implies a greater degree of control is necessary than if a constant ratio were assumed. Second, although there are six alternative models, four are aerometric approaches founded on the same data base and two are smog chamber approaches. Errors or biases in one aerometric model may be shared by the other aerometric models. Similarly, the two smog chamber models have certain approximations and limitations in common. Thus, the uncertainty in the required degree of control may be much greater than indicated by the variance in the numbers presented in Table 5-1.

It should be emphasized that the models reviewed above do not account for contributions from background reactive hydrocarbons, e.g. the geogenic hydrocarbons noted by Crabtree and Mayrsohn, [2]. The existence of background reactive hydrocarbon sources would imply a greater degree of control is required for man-made sources. Since the required degree of overall control is so severe (91 to >95%), and since background contributions may be substantial (up to 13% of total ambient reactive hydrocarbons by weight), a strong argument can be made that even 100% control of the man-made emission inventory will not achieve the oxidant air quality standard in Los Angeles. This argument is highlighted in a very recent paper by Duckworth and McMullen, [15].

The above discussion of the degree of reactive hydrocarbon control required for Los Angeles presents a more pessimistic conclusion than would be reached by the "linear rollback" model. Linear rollback is based on the arbitrary assumption that oxidant levels are directly proportional to reactive hydrocarbon emission levels. The linear rollback model indicates that only 85% reactive hydrocarbon control is required for Los Angeles.

In summary, a great deal of uncertainty surrounds the degree of reactive hydrocarbon control that is necessary to achieve the NAAQS for oxidant in the Los Angeles region. A review of aerometric and smog chamber models indicates that at least 90%, and possibly much higher, control will be required. If background hydrocarbon contributions are accounted for, it appears that even 100% control of man-made sources may not be sufficient.

In view of the uncertainty as to required degree of control, and in view of the potential impossibility of ever attaining the oxidant standard, this report will not derive source emission reductions aimed at actual attainment of the oxidant standard. Rather, for illustrative purposes, 90% reactive hydrocarbon control (for man-made contributions) will be selected as an arbritrary target level. Reactivity criteria will be used to calculate individual source emission reductions corresponding to the overall target level of 90%.

5.2 GUIDELINES FOR DETERMINING INDIVIDUAL SOURCE EMISSION REDUCTIONS

The previous section discussed the overall degree of reactive organic control that would be required to attain the federal oxidant standard in the Metropolitan Los Angeles AQCR. Noting the uncertainties concerning the required degree of emission control and the possibility that even 100% control of man-made organic sources might be insufficient, 90% was arbitrarily chosen as a control target level for the purposes of this study. Having selected an objective for the overall degree of control, the problem remains as to how to allocate emission reductions among individual sources in attaining the overall control level. This section discusses general principles for determining individual source reductions.

Section 5.2.1. points out that the determination of individual source control levels is a classical economic problem. Economic efficiency criteria which govern this allocation problem are described. These criteria are discussed for two cases, indiscriminate control of hydrocarbons and control based on reactivity.

The cost data required to determine source emission reductions based on economic criteria are often unavailable. Section 5.2.2 discusses how source reductions can be allocated in the absence of cost information. Again, both indiscriminate control and control based on reactivity are considered.

5.2.1 Economic Efficiency Principles

The problem of selecting individual source emission reductions that will attain a given level of overall air quality is a classical economic problem. Simply stated, economics is the study of how best to allocate scarce resources among alternative ends in order to attain given objectives. In the problem at hand, we would like to allocate control expenditures among various emission sources in such a way that we minimize total social cost* in attaining a given air quality objective.

Economic theory provides one basic principle for insuring that the allocation of control expenditures is cost efficient. This is the "equality of marginal cost" condition. Let us define the marginal air quality control cost for a source as the extra control cost that will be incurred in attaining one unit of air quality improvement by reducing that emission source. The economic efficiency principle states that the marginal air quality control cost must be the same for all sources. The necessity of this condition in order to minimize total air quality control cost can be proven by a simple contrapositive argument. If the marginal air quality control cost for some source A were less than for some source B, the total social control cost would be lessened (while maintaining the same air quality) by increasing the degree of control on A while relaxing the degree of control on B.

If it is assumed that one ton of emissions from any source has the same impact on air quality (e.g. the indiscriminate approach to controlling hydrocarbons), the marginal air quality control cost condition applies directly to marginal emission reduction costs. Figure 5-9 illustrates this principle for two hypothetical sources (Source I and Source II). For each source, Figure 5-9 presents a total cost curve and marginal control cost curve. The marginal cost curve is simply the negative of the derivative of the total cost curve.

In this hypothetical situation, total emissions are 6 tons per day at the uncontrolled level, 4 tons from Source I and 2 tons from Source II. In order to minimize the total cost of emission control, emission reductions should be carried out such that marginal emission control costs remain the same for each source. For instance, to achieve a 75% overall reduction, Source I should be reduced to point A (.75 tons per day) while Source II should be reduced to point A'(.75 tons per day). To achieve a 90% overall reduction, Source I should be controlled to point B (.25 tons per day) while

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* Actually, the distribution of costs among various economic sectors may also be an important policy consideration. However, the distribution of costs can always be adjusted ex post facto by appropriate transfer payments (e.g. subsidies or taxes). Here we will just address the efficiency criteria of minimizing total resource cost to society.

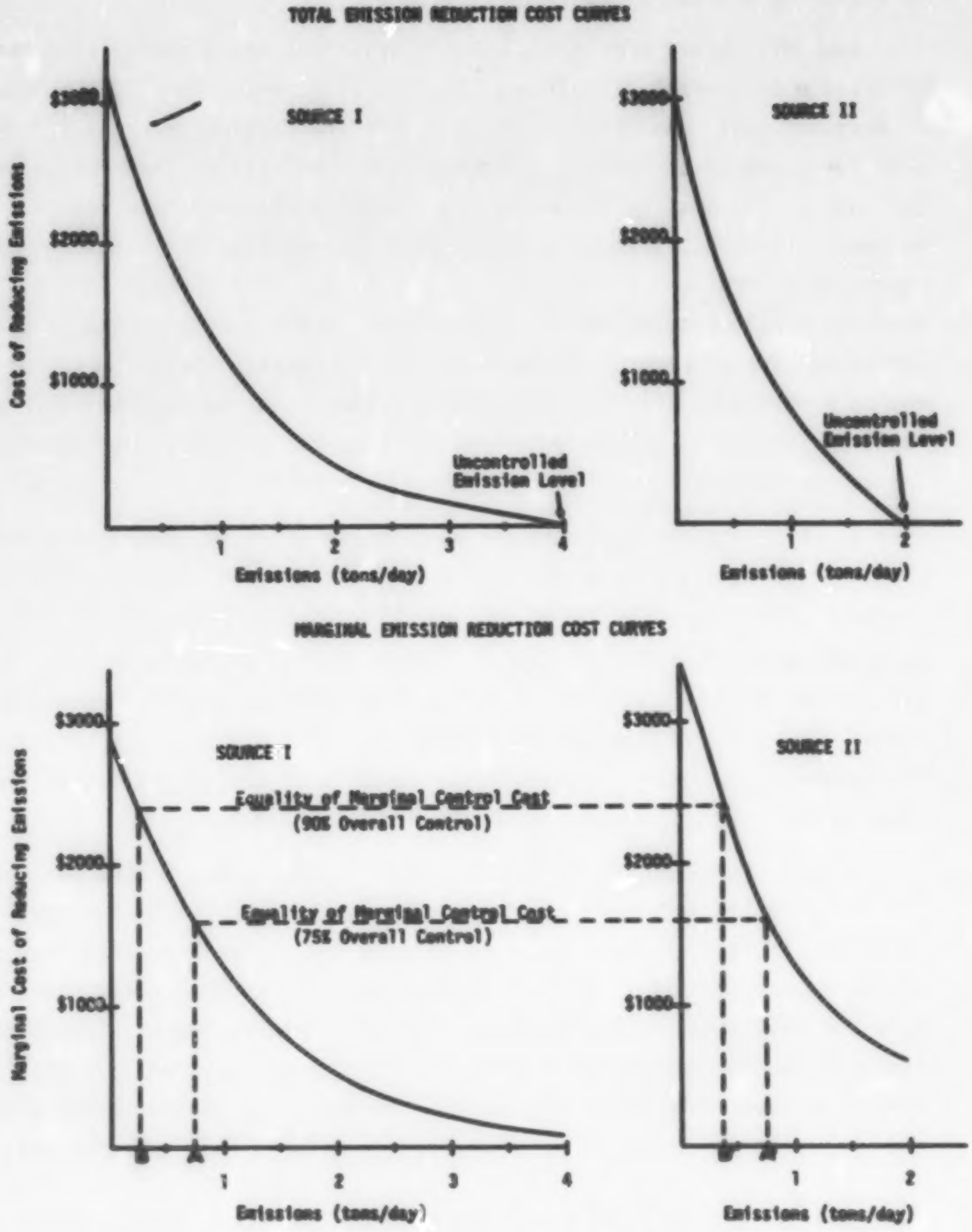

Figure 5-9 . Total and Marginal Control Cost Curves for Two Hypothetical Emission Sources

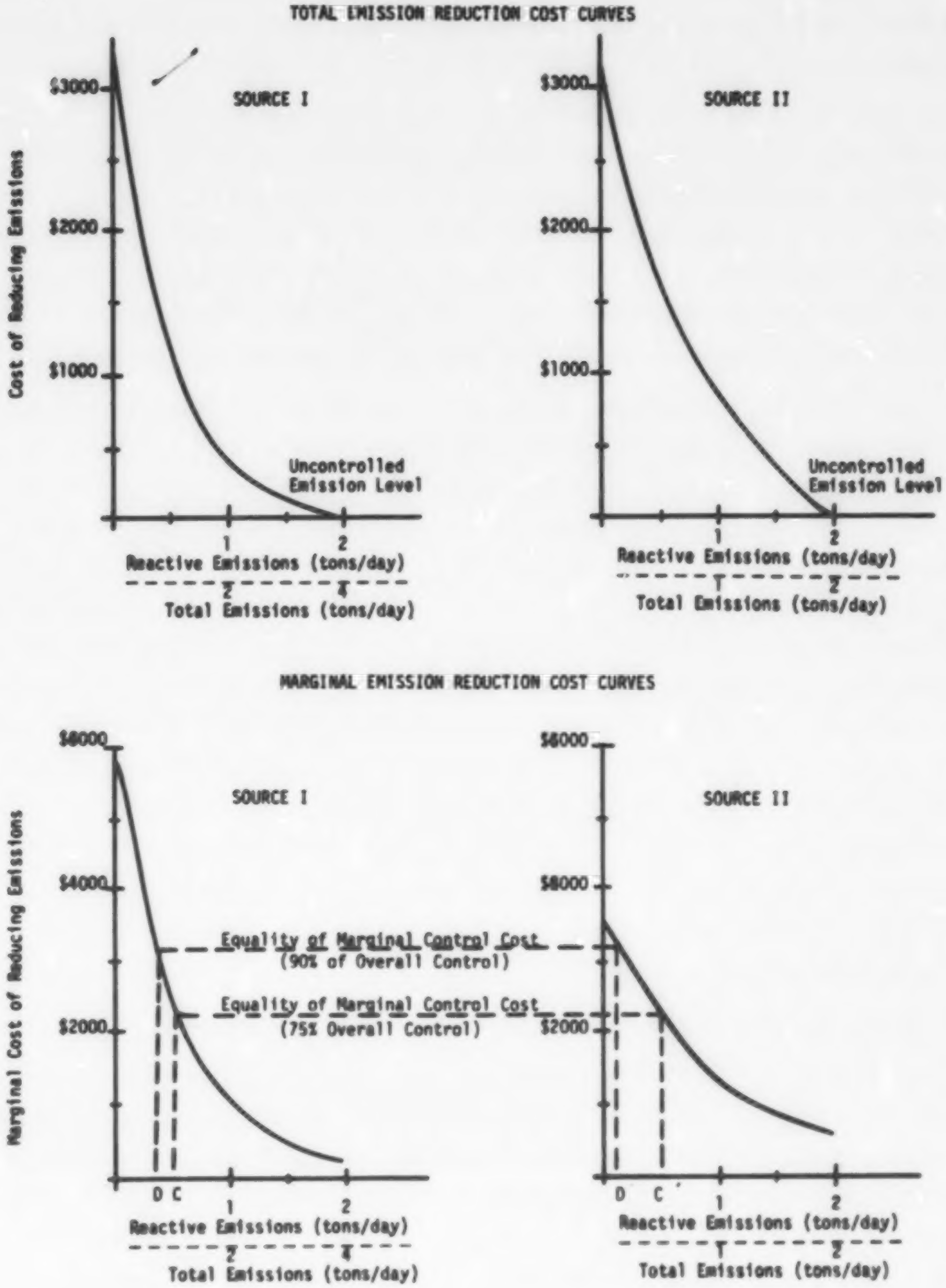

Figure 5-10. Hypothetical Example of Total and Marginal Cost Curves Which Account for Source Reactivity

Source II should be controlled to point B'(.35 tons per day). In this case, Source I is always assigned a greater percentage reduction than Source II because Source I generally exhibits lower marginal control costs.

For the above example, points A-A and B-B were determined by a graphical trial and error technique. In general, the problem of determining cost efficient source emission reductions from individual source control cost curves is a nonlinear mathematical programming problem, [16]. This problem can be approximated by a linear programming problem if piecewise linear total control cost curves are used, [16], [17], [18]. Solutions for real air basins have been obtained using the linear programming approach, [16], [17].

If there is a source-to-source variation in the air quality impact of a given tonnage of emissions, then the marginal cost rule should apply to "effective" emissions rather than total emissions. For instance, if reactivity criteria are considered for hydrocarbons, the efficiency principle would demand that the marginal cost of reactive emission reductions be equal for all sources. If it were assumed that Source I has a weight reactivity of 0.5 and Source II has a weight reactivity of 1.0 in the hypothetical example above, then the appropriate marginal cost curves would be as shown in Figure 5-10. Of course, accounting for reactivity would alter the relative degrees of control required for each source, (compare points C-C' to A-A and D-D' to B-B'). The concept of "effective" emissions might be used for other pollutants (e.g. SO_2, NO_x, TSP, etc.) if the spatial distribution of emissions produces source-to-source variations in air quality impact per ton. For instance, tall stack or nonurban emissions might be weighted less than ground level or urban emissions.

5.2.2 Source Emission Reductions in the Absence of Control Cost Information

The previous section discussed economic guidelines for determining individual source reductions which attain a given overall degree of control. To apply these guidelines requires knowledge of the relationship between control costs and emission reductions for each source. Such cost information is often unavailable, and it is useful to discuss rules for allocating individual source emission reductions when cost knowledge is lacking.

First, let us consider the case where emissions from all sources have the same impact (per ton) on air quality, e.g. the indiscriminate approach to organic control. In this case, it is reasonable and equitable (in the absence of control cost data for individual sources) to allocate the same degree of control to each source. Thus, if C were the overall degree of control required, individual source emission reductions would each be specified by

$$\frac{E_i^0 - E_i}{E_i^0} = C \quad \text{for} \quad i=1,\ldots,N, \qquad (5\text{-}3)$$

where

E_i^0 = weight emissions from the ith source before control,

E_i = weight emissions from the ith source after control,

and N = total number of sources.

Of course, equation (5-3) would automatically insure that the overall degree of control would be C since, by simple linearity,

$$\begin{aligned} \text{Total emissions after control} &= \sum_{i=1}^{N} E_i \\ &= \sum_{i=1}^{N} (E_i^0 - E_i^0 C) \quad \text{by (5-3)} \\ &= (1-C) \sum_{i=1}^{N} E_i^0 \\ &= (1-C)(\text{total emissions before control}). \end{aligned}$$

Next let us examine the case of source-to-source variation in the air quality impact per ton of emissions. For instance, let us consider the use of reactivity criteria in organic control, with SWR_i representing the source weight reactivity for the ith source. In the absence of control cost information, there appears to be one* simple and reasonable control allocation rule that accounts for varying reactivities. This rule is that each source should be controlled so that the fraction of emissions remaining is inversely proportional to the reactivity of the source, or stated symbolically,

$$\frac{E_i}{E_i^o} = \frac{K}{SWR_i} \quad \text{for} \quad i=1,\ldots,N, \tag{5-4}$$

In this case, the constant (K) is determined by insuring that the overall degree of reactive organic control is C. This is accomplished as follows:

$$\begin{aligned}
1-C &= \frac{\text{total reactive emissions after control}}{\text{total reactive emissions before control}} \\
&= \frac{\sum_{i=1}^{N} SWR_i E_i}{\sum_{i=1}^{N} SWR_i E_i^o} \\
&= \frac{K \sum_{i=1}^{N} E_i^o}{\sum_{i=1}^{N} SWR_i E_i^o} \qquad \text{by (5-4)} \\
&= K/\overline{SWR}^o
\end{aligned}$$

where

$\overline{SWR}^o$ = average source weight reactivity before control.

---

* The reader will find that other control allocation rules are either overly complex or yield unreasonable results. For instance, the simple rule that "each source be controlled in proportion to its reactivity" may require that more than 100% control be established for some sources.

Thus, we have,

$$K = (1-C)\overline{SWR^o}. \tag{5-5}$$

Combining equations (5-4) and (5-5) yields the following control allocation rule:

$$\frac{E_i}{E_i^o} = \frac{(1-C)\overline{SWR^o}}{SWR_i}, \quad \text{for } i=1,\ldots,N \tag{5-6}$$

5.3 EMISSION REDUCTIONS FOR ORGANIC SOURCES IN THE METROPOLITAN LOS ANGELES AQCR

Section 5.1 discussed the overall degree of reactive organic control required to attain the national oxidant standard in the Metropolitan Los Angeles AQCR. Section 5.2 presented guidelines for allocating emission reductions among individual sources in achieving a given degree of overall emission control. These guidelines included economic efficiency criteria (Section 5.2.1) as well as equity criteria which could be used in absence of economic data (Section 5.2.2). Based on these results, the present section determines individual emission reductions for organic sources in the Metropolitan Los Angeles AQCR.

The use of economic efficiency guidelines in establishing individual source control levels requires knowledge of the relationship between emission reductions and control costs for each source category. For this study of organic control in Los Angeles, emission control cost curves are not available for most source types. Some information exists concerning the cost of specific controls for major source types [16], but present data are insufficient to establish complete cost curves in most cases. To assemble detailed control cost information is not possible within the resources allocated to this project. Thus, the equity criteria of Section 5.2.2 will be used to allocate control among individual sources rather than the economic efficiency criteria of Section 5.2.1.

Table 5-2 summarizes control requirements for individual organic source categories in the Metropolitan Los Angeles AQCR. These control requirements are based on the arbitrary target level of 90% overall reactive organic control.

Allowable emissions and percent reductions are listed for indiscriminate organic control as well as for control based on three reactivity classification schemes: the 2-group, 5-group, and 6-group schemes (see Chapters 1 and 4 for descriptions of these reactivity scales).

For indiscriminate organic control, source emission reductions are calculated from equation (5-3); accordingly, each source is reduced by 90%. For each reactivity classification scheme, source emission reductions are determined from equation (5-6). As evidenced by Table 5-2, sources with high reactivity are assigned the greatest emission reductions. The two sources with extremely low reactivity, PCE drycleaning and 1,1,1-T degreasing, are actually assigned increased emissions (over uncontrolled levels) by formula (5-6).

A very notable feature of Table 5-2 is that emission reductions are quite stringent for nearly all source categories under each reactivity scheme. Twenty-one of the twenty-six source categories are allocated degrees of control ranging from 85% to 94% by all three reactivity schemes. Three other source categories (petroleum production, stationary source fuel combustion, and petroleum based dry cleaning solvent) are allocated somewhat lesser control levels, generally about 80%. As noted above, PCE dry cleaning and 1,1,1-T degreasing are allowed to increase emissions.

The general uniformity in the degree of control assigned to most source categories is a result of two factors. First, as discussed in Chapter 4, there is a uniformity in reactivity ratings among most source categories. Second, the very stringent degree of overall control (90%) requires that almost all sources be controlled to very high levels.

Table 5-3 lists individual source emission reductions for various degrees of overall control, ranging from 10% to 95%. These have been computed from equation (5-6), with source weight reactivities based on the 5-group reactivity classification scheme. At high levels of overall control (>50%), the general uniformity of control requirements among most source categories is again apparent. At very low levels of overall control (<20%), several source categories with low reactivity are allowed to increase emissions according to formula (5-6).

TABLE 5-2. INDIVIDUAL SOURCE EMISSION REDUCTIONS FOR 90% OVERALL DEGREE OF CONTROL

SOURCE CATEGORY	TOTAL 1972 EMISSIONS TONS/DAY	SOURCE WEIGHT REACTIVITIES			ALLOWABLE EMISSIONS* - TONS/DAY (90% OVERALL DEGREE OF CONTROL)				PERCENT REDUCTIONS (90% OVERALL DEGREE OF CONTROL)			
		2-GROUP SCHEME	5-GROUP SCHEME	6-GROUP SCHEME	[illegible]	2-GROUP SCHEME	5-GROUP SCHEME	6-GROUP SCHEME	[illegible]	2-GROUP SCHEME	5-GROUP SCHEME	6-GROUP SCHEME
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION												
Petroleum Production and Refining												
Petroleum Production	62	.30	.45	.29	6	11	9	13	90%	82%	85%	79%
Petroleum Refining	50	.66	.53	.58	5	5	6	5	90%	90%	88%	90%
Gasoline Marketing												
Underground Service Station Tanks	48	.96	.88	.88	5	3	4	4	90%	94%	92%	92%
Auto Tank Filling	108	.90	.73	.78	10	8	9	9	90%	92%	91%	91%
Fuel Combustion	23	.20	.55	.33	2	6	3	4	90%	74%	87%	83%
Waste Burning & Fires	41	.56	.77	.67	4	5	3	4	90%	88%	93%	90%
STATIONARY SOURCES: ORGANIC CHEMICAL												
Surface Coating												
Heat Treated	14	.67	.59	.59	1	1	2	1	90%	93%	86%	93%
Air Dried	129	.68	.55	.55	13	13	15	15	90%	90%	88%	88%
Dry Cleaning												
Petroleum Based Solvent	16	.55	.36	.36	2	2	3	3	90%	87%	81%	81%
Synthetic Solvent (PCE)	25	.00	.04	.04	3	**	40	39	90%	**	-60%	-56%
Degreasing												
TCE Solvent	11	.52	.50	.50	1	1	1	1	90%	91%	91%	91%
1,1,1-T Solvent	95	.00	.05	.05	10	**	122	120	90%	**	-28%	-26%
Printing												
Rotogravure	31	.69	.52	.52	3	3	4	4	90%	90%	87%	87%
Flexographic	15	.96	.92	.92	1	1	1	1	90%	93%	93%	93%
Industrial Process Sources												
Rubber & Plastic Manf.	42	.79	.92	.93	4	4	3	3	90%	90%	93%	93%
Pharmaceutical Manf.	16	.61	.59	.59	2	2	2	2	90%	87%	87%	87%
Miscellaneous Operations	83	.68	.66	.66	8	12	12	11	90%	86%	86%	87%
MOBILE SOURCES												
Gasoline Powered Vehicles												
Light Duty Vehicles												
Exhaust Emissions	700	.72	.72	.72	70	73	69	68	90%	90%	90%	90%
Evaporative Emissions	481	.72	.61	.61	48	45	50	50	90%	91%	90%	90%
Heavy Duty Vehicles												
Exhaust Emissions	285	.72	.72	.72	28	27	28	25	90%	91%	90%	91%
Evaporative Emissions	67	.72	.61	.61	7	6	7	7	90%	91%	90%	90%
Other Gasoline Powered Equipment												
Exhaust Emissions	110	.72	.72	.72	11	10	10	10	90%	91%	91%	91%
Evaporative Emissions	22	.72	.61	.61	2	2	2	2	90%	91%	91%	91%
Diesel Powered Motor Vehicles	12	.67	.79	.79	1	1	1	1	90%	92%	92%	92%
Aircraft												
Jet	20	.52	.90	.90	2	3	3	3	90%	90%	90%	90%
Piston	22	.81	.91	.89	2	2	2	2	90%	91%	91%	91%
TOTAL OR WEIGHTED AVERAGE	2660	.67	.64	.63	266	--	400	407	90%	--	84.3	84.4

* Calculated according to equation (5-6)

** Equation (5-6) assigns infinite allowable emissions in this case

TABLE 5-3. INDIVIDUAL SOURCE EMISSION REDUCTIONS FOR VARIOUS DEGREES OF OVERALL CONTROL (ACCORDING TO THE 5-GROUP SCHEME)

SOURCE CATEGORY	PERCENT REDUCTIONS FOR VARIOUS DEGREES OF OVERALL CONTROL									
	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%
STATIONARY SOURCES: ORGANIC FUELS AND COMBUSTION										
Petroleum Production and Refining										
Petroleum Production	-27	-15	0	15	29	44	58	71	86	94
Petroleum Refining	-8	4	16	28	40	52	64	76	88	94
Gasoline Marketing										
Underground Service Station Tanks	31	40	46	54	63	69	77	86	92	96
Auto Tank Filling	21	30	38	47	56	65	74	83	91	95
Fuel Combustion	-4	9	17	30	43	52	65	78	87	96
Waste Burning & Fires	24	29	41	51	59	66	76	83	93	95
STATIONARY SOURCES: ORGANIC CHEMICALS										
Surface Coating										
Heat Treated	0	14	21	36	43	57	64	79	86	93
Air Dried	-5	7	19	30	42	53	65	77	88	94
Dry Cleaning										
Petroleum Based Solvent	-63	-44	-25	-6	13	31	44	63	81	94
Synthetic Solvent (PCE)	-1340	-1180	-1020	-860	-700	-540	-380	-220	-60	20
Degreasing										
TCE Solvent	-18	0	9	27	36	45	64	73	91	91
1,1,1-T Solvent	-1052	-924	-796	-668	-540	-412	-284	-156	-28	36
Printing										
Rotogravure	-10	0	13	26	39	52	65	74	91	94
Flexigraphic	40	47	53	60	67	73	80	87	93	93
Industrial Process Sources										
Rubber & Plastic Manf.	38	45	52	57	64	71	79	86	93	98
Pharmaceutical Manf.	0	13	25	38	44	56	69	81	87	94
Miscellaneous Operations	-25	-11	2	17	30	45	58	72	86	93
MOBILE SOURCES										
Gasoline Powered Vehicles										
Light Duty Vehicles										
Exhaust Emissions	20	29	38	47	56	64	73	82	91	96
Evaporative Emissions	0	16	27	37	48	58	69	79	90	96
Heavy Duty Vehicles										
Exhaust Emissions	20	29	38	47	55	65	73	82	91	95
Evaporative Emissions	0	16	27	37	48	58	69	79	90	94
Other Gasoline Powered Equipment										
Exhaust Emissions	20	29	38	46	55	65	74	82	91	95
Evaporative Emissions	0	18	27	36	45	59	68	77	91	95
Diesel Powered Motor Vehicles	25	33	42	50	58	67	75	83	92	96
Aircraft										
Jet	-15	0	10	26	35	50	60	75	85	95
Piston	36	45	50	59	64	73	77	86	91	95

5.4 REFERENCES

1. W. J. Hamming, R. L. Chass, J. E. Dickinson, and W. G. MacBeth, "Motor Vehicle Control and Air Quality, The Path to Clean Air for Los Angeles", Paper by the Los Angeles County Air Pollution Control District, Presented at the 66th Annual Meeting of the Air Pollution Control Association, Chicago, Illinois, June 1973.

2. H. Mayrsohn and J. Crabtree, "Source Reconciliation of Atmospheric Hydrocarbons", California Air Resources Board Division of Technical Services, Paper Submitted to Atmospheric Environment, March 1975.

3. U. S. Environmental Protection Agency, "Air Quality Criteria for Photochemical Oxidants", Publication No. AP-63, March 1970.

4. J. C. Trijonis, G. Richard, K. Crawford, R. Tan, and R. Wada, "An Implementation Plan for Suspended Particulate Matter in the Los Angeles Region", Prepared for the Environmental Protection Agency, Contract No. 68-02-1384, TRW Environmental Services, Redondo Beach, California, March 1975.

5. W. B. DeMore, "LAAPCD Method More Accurate, ARB More Precise", California Air Resources Board Bulletin, Vol. 5 No. 11, December 1974.

6. E. A. Schuck and R. A. Papetti, "Examination of the Photochemical Air Pollution Problem in the Southern California Area", EPA Internal Working Paper, May 1973.

7. Federal Register, Volume 36, No. 158, August 14, 1971

8. E. A. Schuck, A. P. Altshuller, D. S. Barth, and G. B. Morgan, "Relationship of Hydrocarbons to Oxidants in Ambient Atmospheres", Journal of the Air Pollution Control Association, Vol 20, No. 5, May 1970.

9. P. H. Merz, L. J. Painter, and P. R. Ryason, "Aerometric Data Analysis - Time Series Analysis and Forecast and an Atmospheric Smog Diagram", Atmospheric Environment, Vol. 6, p. 319, 1972.

10. J. R. Kinosian and J. J. Paskind, "Hydrocarbons, Oxides of Nitrogen, and Oxidant Trends in the South Coast Air Basin, 1963-1972", California Air Resources Board - Division of Technical Services, Internal Working Paper.

11. California Air Resources Board Division of Technical Services, "Ten Year Summary of California Air Quality Data, 1963-1972", January 1974.

12. J. C. Trijonis, "Economic Air Pollution Control Model for Los Angeles County in 1975", Environmental Science and Technology, Vol. 8, No. 9, September 1974.

13. B. Dimitriades, "Effects of Hydrocarbons and Nitrogen Oxides on Photochemical Smog Formation", Environmental Science and Technology, Vol. 6 1972.

14. B. Dimitriades, "Development of an Oxidant Abatement Strategy Based on Smog Chamber Data", Internal Working Paper, EPA Chemistry and Physics Laboratory, August 1973.

15. S. Duckworth and R. W. McMullen, "Can We Ever Meet the Oxidant Standard?", Presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston, Massachusetts, June 1975.

16. J. C. Trijonis, An Economic Air Pollution Control Model - Application: Photochemical Smog in Los Angeles County in 1975, Ph.D. Thesis, California Institute of Technology, May 1972.

17. R. Kohn, "A Linear Programming Model for Air Pollution Control: A Pilot Study of the St. Louis Airshed, Journal of Air Pollution Control Association, Vol. 20, 1970, pp. 78-82.

18. S. E. Atkinson and D. H. Lewis, "A Cost Evaluation of Alternative Air Quality Control Strategies," EPA Report No. EPA-600/5-74-003, January 1974.

6.0 EVALUATION OF ALTERNATIVE APPROACHES TO ORGANIC EMISSION CONTROL

The present chapter briefly evaluates the benefits and costs associated with using reactivity criteria to formulate organic control strategies. The basic benefit in using reactivity criteria in organic emission control consists of increased flexibility. Reactivity criteria introduce the possibility of selective emission control as a potentially advantageous alternative to the less flexible approach of indiscriminate control. The costs of using reactivity criteria are extra administrative and testing expenditures. This chapter provides a very approximate assessment of these benefit/cost trade-offs.

Three alternative approaches to organic control will be considered here, indiscriminate control and two reactivity based policies. Indiscriminate control neglects source-to-source variations in reactivity. The first reactivity based policy involves establishing emission standards for each source category based on reactivity ratings. In this policy, emission standards are to be achieved by reducing total emissions. The second reactivity based policy also establishes emission standards based on reactivity. However, the second policy allows standards to be attained by substitutive controls* as well as by total emission reductions.

Section 6.1 evaluates the benefits and costs of the first reactive policy as compared to indiscriminate control. Section 6.2 assesses the extra benefits and costs of the second reactive policy as compared to the first reactive policy. Section 6.3 provides a brief summary and discussion of the trade-offs.

6.1 ORGANIC EMISSION STANDARDS BASED ON REACTIVITY WITH NO SUBSTITUTIVE CONTROLS

The first level of sophistication in applying reactivity criteria to organic control policy is to establish emission standards for various source categories based on present reactivity ratings. Sources with high reactivity would be assigned a greater degree of control than sources of lesser reactivity (see Table 5-2 for example). Each emission source category would be required to attain the standards by reducing total emissions, not by substituting less reactive compounds for more reactive compounds.

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* Substitutive control for an organic emission source involves the replacement of reactive constituents with less reactive organics so as to lower the reactivity rating of the source.

This type of reactivity based strategy would have the benefit of concentrating emissions reductions among the most reactive sources. This would allow a given reduction in reactive emissions to be attained with lesser control of total emissions than would be called for by indiscriminate organic control. In essence, more total hydrocarbons would be emitted (while maintaining the same air quality) by adopting this reactivity based approach. Of course, the reactivity based strategy would also involve extra costs as compared to the indiscriminate approach. These would be the administrative and testing costs involved in determining reactivities for various source categories. The benefits and costs of applying this approach to reactive organic control in the Metropolitan Los Angeles AQCR are discussed in Sections 6.1.1 and 6.1.2, respectively.

6.1.1 Benefits of the Reactivity Based Strategy with No Substitutive Controls

There is only one rigorous way to assess the economic benefits of establishing organic emission standards based on reactivity. The cost of attaining the stipulated emission reductions for each source category should be determined for both the reactivity based strategy and the indiscriminate strategy. The total cost of control (the sum of the costs for all sources) should then be compared for the two strategies. The economic benefit of the reactivity based approach, as compared to the indiscriminate approach, would be the savings in total strategy control costs.

In order to perform this assessment of economic benefits, information on emission reduction costs would be required for every source category. This is exactly the same type of control cost information that is necessary to allocate source emission reductions based on economic efficiency criteria (see Section 5.2.1). As noted in Chapter 5, these cost data are not available for most organic source categories in the Metropolitan Los Angeles AQCR. Thus, we cannot perform a rigorous analysis of the economic benefits of a reactivity based approach for the same reason that we could not use economic efficiency guidelines in allocating individual source emission reductions.

Fortunately, the results of Tables 5-2 and 5-3 allow a simplified interpretation of the economic benefits associated with the reactivity approach. Table 5-2 indicates an obvious saving from the reactivity based approach at 90% control; 148 more tons per day of emissions are allowed with the (5-group) reactivity based strategy than with the indiscriminate strategy. The benefit from the reactivity based approach is the expenditure that is saved by not having to control this 148 tons/day.

A close examination of Table 5-2 reveals that the 148 tons/day saving essentially involves only two sources, PCE dry cleaning and 1,1,1-T degreasing. These sources are allowed to emit 162 tons per day under the 5-group reactivity strategy, whereas they would be allowed only 13 tons/day under the indiscriminate strategy. Although there are some source-to-source variations in control levels among the other 24 source categories, the other 24 categories as a whole are controlled by 90% in the reactivity based strategy as well as in the indiscriminate strategy. Thus, for 90% overall control, the benefit from the reactivity based strategy is essentially that PCE dry cleaning and 1,1,1-T degreasing need not be controlled.

An analysis of the results of Table 5-3 indicates that the above conclusion also holds for other degrees of control (from 10% to 95%). The 24 source categories (sources other than PCE dry cleaning and 1,1,1-T degreasing) as a whole are controlled to the same degree in the reactivity based strategy as in the indiscriminate strategy. Thus, the one basic benefit from the reactivity approach is not controlling the two source categories of very low reactivity. This is apparently a consequence of the general uniformity in reactivity ratings among the other 24 source categories.

6.1.2 Costs of the Reactivity Based Strategy with No Substitutive Controls

This section will consider the program requirements and associated program costs of adopting reactivity based organic emission regulations. The discussion of program requirements consists of an outline of the basic activities that are necessary for the implementation and operation of reactivity based emission regulations. The costs of these activities are described only in a very qualitative way. Since it is very difficult to estimate costs accurately, showing probable upper and lower bounds seems most appropriate. It is, in fact, difficult to assess accurately what the costs of past programs have been, [1]..

For the purposes of this discussion, it is assumed that the regulations will apply to each type of industry based on the industry average reactivity, not on the reactivity of individual plants. That is, the average reactivity for all the plants in an industry will be used to establish emission regulations for each individual plant in that industry. It is also assumed that the regulations will be administered by a local governmental unit, such as a county Air Pollution District. Another tacit assumption is that a suitable reactivity scale will exist that includes all types of compounds.

There are two types of program requirements and costs for implementing reactivity based emission regulations. The first includes those activities that are performed only once, (or only occasionally), such as determining the composition of the organic emissions for the various source types. The second involves continuing operating activities, such as enforcement.

Prior to establishing new regulations, compositional data on the emissions from each type of organic source must be obtained. As evidenced by Chapter 3, the open literature probably will not provide sufficient data to determine compositions accurately enough for regulatory purposes. This indicates that a substantial test program will be necessary. The test program will have to analyze the composition of a statistically significant number of each type of source in order to account for the differences that exist between one plant and another in the same type of industry.

It should be noted that obtaining composition data for some source types will probably have to be performed separately for each jurisdictional area, since previous emission regulations may vary from area to area. Previous emission regulations in some areas may have altered source compositions from the norm (see Section 3.3.1 which describes how the composition of paint solvents is different in Los Angeles than elsewhere in the nation because of local regulations). The mix of process type may also vary from area to area.

In the present case, emission regulations will be met by total emission reductions and not by substitutive controls. Thus, the enforcement function will be essentially the same as the case of indiscriminate control. Accordingly, enforcement costs will be the same as for indiscriminate control.

Table 6-1 shows the approximate costs of the activities necessary to establish reactivity based emission regulations. For the present case, the costs are essentially just the expenses of determining source compositions. Also shown in Table 6-1 are the annualized, initial costs amortized over 5 years and 20 years. The 5 year values are shown because it is possible that the regulations will be reviewed every 5 years in order to determine changes in the composition of the emissions as changes in technology occur. The 20 year values are shown for the case where 5 year reviews are not conducted. A basic assumption in Table 6-1 is that the necessary source testing and analysis would be contracted to the private sector. This seems the most likely approach since the tests would only be performed on one occasion and would require expensive and specialized equipment which would not be necessary for normal control agency operations.

TABLE 6-1. ESTIMATED COSTS FOR ESTABLISHING REACTIVITY BASED ORGANIC EMISSION REGULATIONS

Program Requirement	Composition Data	
Initial Cost .... (100 to 500 tests at $500 to $1,000 per test)	$50,000 to $500,000	
Annualized Cost Over 5 Years*	$13,200 to $131,900	Per Year
Annualized Cost Over 20 Years*	$5,900 to $58,700	Per Year

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* Using $I_n = I\left(\frac{i}{(1+i)^n-1} + i\right)$, where i = 10% (interest rate), n = years lifetime of the program, In = the original cost, and I_n = annualized cost.

6.2 ORGANIC EMISSION STANDARDS BASED ON REACTIVITY WITH SUBSTITUTIVE CONTROLS

The second reactivity based approach to organic emission control allows substitutive control measures in addition to establishing emission standards based on reactivity. Allowing substitutive control measures increases the number of potential control options. Extra benefits are accrued from this approach whenever the substitutive control options are less expensive than emission reduction controls. Increased costs with this approach result from additional administrative and testing requirements. The extra benefits and costs of applying this second reactivity based strategy to the Metropolitan Los Angeles AQCR are discussed in Sections 6.2.1 and 6.2.2, respectively.

6.2.1 Benefits of the Reactivity Based Strategy with Substitutive Controls

An accurate evaluation of the benefits from allowing substitutive controls would require detailed documentation of substitutive control alternatives and emission reduction control alternatives for each source category. Benefits would arise whenever substitutive control measures (either alone or in conjunction with emission reduction measures) allow a given degree of control to be attained at less expense than pure emission reduction measures. These benefits should be summed over all source categories.

As noted previously, the data to perform a comprehensive cost analysis of alternative control options are not available for most source categories. In the absence of data for a thorough evaluation, we can only describe the potential benefits in a qualitative manner. The discussion below gives a very general assessment of potential benefits from substitutive controls.

An examination of the source categories in the present organic inventory for Los Angeles reveals two cases where substitutive controls have yielded substantial reductions in reactivity. These are the substitution of 1,1,1-T degreaser for TCE degreaser and the substitution of PCE dry cleaning solvent for petroleum based dry cleaning solvent. 1,1,1-T degreaser has weight reactivities of .00, .05, and .05 according to the 2-group, 5-group, and 6-group classification schemes, respectively, while TCE degreaser has weight reactivities of .52, .50, and .50. PCE dry cleaning solvent has weight reactivities of .00, .04, and .04, while petroleum dry cleaning solvent rates at .55, .36, and .36. In each case, a synthetic solvent (1,1,1-T or PCE) was used to perform the substitution.

Because of APCD Rule 66, some substitution control has also been carried out among other solvent categories, in particular air dryed surface coating. However, from the present reactivity ratings of these other solvent sources (see Table 4-2) it does not appear that the reductions in reactivity were very large (at least as measured by the oxidant reactivity schemes used here). For instance, air dried surface coating still rates at .68, .55 and .55 according to the 2-group, 5-group and 6-group schemes. These values are nearly as great as the average reactivity for all sources. It is interesting to note that, in this case, one petroleum based solvent was substituted for another petroleum based solvent.

As a gross generality, it appears that large reductions in reactivity cannot usually be achieved by substituting one petroleum product for another. To attain large reductions in reactivity apparently requires major substitution of Class I compounds for compounds in Classes III to V. This would usually be practical only by switching to synthetic solvents (e.g., PCE dry cleaner or 1,1,1-T degreaser) or by converting to gaseous fuels (e.g., methane or methanol). Substitution of Class II compounds does not generally seem practical because Class II compounds are rare. Substitution of one petroleum product for another would usually be restricted to replacing Class IV and V compounds (e.g., olefins and aromatics) by Class III compounds (e.g., C_4^+ parafins). Table 6-2 illustrates that replacement of all Class IV and V compounds with Class III compounds would not have extreme effects on the reactivities of solvents, gasoline engine exhaust or evaporated gasoline.

The conclusion that substituting one petroleum product for another will generally not yield substantial reductions in reactivity is also supported by the uniformity in source weight reactivities noted in Section 4.2. Table 4-2 illustrated that reactivity ratings changed little among all the varied uses of petroleum solvents and petroleum fuels. Among sources involving petroleum based solvents or fuels, weight reactivities varied only from about .5 to .9.

It should be noted that substitution of low reactivity compounds may not be feasible for many petroleum based solvents if these solvents are to retain their utility. For instance, the substitution of lesser

TABLE 6-2. THE EFFECT OF SUBSTITUTING CLASS III COMPOUNDS FOR CLASS IV AND CLASS V COMPOUNDS IN SEVERAL SELECTED SOURCE CATEGORIES

SOURCE CATEGORY	PRESENT COMPOSITION (MOLE %) CLASS I	CLASS II	CLASS III	CLASS IV	CLASS V	POTENTIAL REACTIVITY REDUCTION FROM REPLACEMENT OF ALL CLASS IV AND CLASS V COMPOUNDS BY CLASS III COMPOUNDS
Surface Coating						
Heat Treated	20	0	28	50	2	24%
Air Dried	14	0	52	29	5	19%
Dry Cleaning						
Petroleum Based Solvent	0	0	94	5	1	3%
Printing						
Rotogravure	16	0	61	23	0	11%
Flexigraphic	19	0	8	73	0	29%
Industrial Process Sources						
Rubber & Plastic Manufacturing	16	1	24	7	52	44%
Pharmaceutical Manufacturing	34	1	5	60	0	30%
Miscellaneous Chemical Manufacturing	44	0	29	18	9	25%
Gasoline Powered Vehicles (All)						
Exhaust Emissions	28	0	30	19	23	32%
Evaporative Emissions	5	0	58	21	16	24%

reactives in surface coatings (under APCD Rule 66) has already been carried out to the extent that further substitutions might produce deterioration in performance. Thus, not only will substitution of lower reactivity petroleum compounds have limited effect, but also it may be costly in terms of performance losses.

To summarize, the utility of substitutive controls in attaining substantial reductions in reactivity will be mostly limited to the use of synthetic solvents or gaseous fuels which have near zero reactivity. The substitution of lesser reactive petroleum products (e.g., C_4^+ paraffins) for highly reactive petroleum products (e.g., aromatics) will usually not result in major reductions in source reactivities and may be associated with high costs in terms of product performance. Accordingly, the benefit from allowing substitutive controls will be most significant for sources where synthetic solvents or gaseous fuels are a viable control measure.

6.2.2 Costs of the Reactivity Based Strategy with Substitutive Controls

This section considers the extra program requirements and program costs of allowing substitutive controls. The extra program requirements (in addition to those described in Section 6.1.2) are increased laboratory and field test capabilities. The increased costs are for additional equipment and personnel.

The type of regulation being discussed allows compliance by substitution of low reactivity compounds for high reactivity ones as well as by emission reduction measures. Because of this, the allowable emissions would have to be recalculated each time the process causing the emissions changes.

The additional program requirements involve upgrading laboratory and field test capabilities and increasing the number of tests to be run. Although most air pollution control agencies already have some laboratory facilities, in most cases, they would not have the necessary equipment or personnel to conduct the much more sophisticated analyses that this type of enforcement program would require. Similarly, the actual taking of the sample at the emission source would be more complicated and would probably require new equipment. Since the number of source tests would most likely be increased, the number of source test personnel would probably have to be increased also.

Since the composition of the emissions from each individual source would become important, the field testing requirements might become prohibitive if only the local agency could certify the composition and thereby set the legal mass emission rate. Because of this, it is probable that provisions would be made in the law which would allow qualified private testing labs to conduct the testing and analysis at the expense of the plant operator. This would be to the advantage of both the agency and the operator in the cases where a large backlog of testing was forcing the operator to comply with more restrictive mass based regulations.

It is also conceivable that a dual system could be instituted whereby a mass emission rate is set for all sources in a given type of industry subject to being made less restrictive when analysis showed that the reactivity was sufficiently low. In this case, the burden of proof would lie with the operator. Under this system the costs to the control agency would be reduced since the testing costs would be transferred to the source operators.

Table 6-3 shows the anticipated additional costs for enforcing regulations which allow substitution of low reactivity compounds for high reactivity ones. These costs are calculated based on the assumption that all tests are conducted by the control agency.

6.3 IMPLICATIONS OF THE BENEFIT/COST EVALUATION

The previous two sections briefly evaluated the costs and benefits associated with alternative approaches to organic control policy in Los Angeles. Section 6.1 compared indiscriminate organic control to a reactivity based policy which establishes emission standards based on present source reactivities but which does not allow substitutive controls. It was noted that the reactive policy generally would yield the benefit of concentrating emission reductions among the most reactive sources. This would allow more total organics to be emitted for a given degree of overall control. However, for Los Angeles, this benefit translated only into relaxing controls on PCE dry cleaning and 1,1,1-T degreasing. The extra administrative and testing costs for this reactive strategy (over an

TABLE 6-3. COSTS OF THE SECOND REACTIVITY BASED POLICY

PROGRAM REQUIREMENT	INITIAL COST	ADDITIONAL OPERATING COSTS	INITIAL COSTS ANNUALIZED OVER 20 YEARS; $/YEAR	TOTAL ANNUAL COST	COMMENTS
Additional Testing and Analysis Equipment	$0 - $75,000	---	$0 - $8800	$0 - $8800	
Additional Test and Laboratory Personnel	---	$125,000 - $250,000	---	$125,000 - $250,000	5 to 10 extra man-years per year; cost based on average man-year expense of $25,000 per year*.
TOTAL	$0 - $75,000	$125,000 - $250,000	$0 - $8800	$125,000 - $258,800	

*This includes salary, fringe benefits and overhead; based on data from the Los Angeles County Air Pollution Control District,[2].

indiscriminate control policy) were estimated to be about $10,000 to $100,000 on an annualized basis.

Section 6.2 compared the first reactivity based policy to a second one which establishes emission standards based on reactivity and allows substitutive controls. The extra benefit of this policy (as compared to the first reactive policy) consisted of increased flexibility in selecting among alternative control measures. The increase number of control options introduced the possibility of reducing the costs of control. For organic sources in Los Angeles, it was noted that large reductions in reactivity probably could not be attained by substituting one petroleum product for another. The benefits of substitutive controls apparently would be substantial only for those sources which could attain very low reactivity by conversion to synthetic solvents or gaseous fuels. The extra costs of this reactive policy (as compared to the first reactive policy) were estimated to be about $100,000 to $250,000 on an annualized basis.

Definitive recommendations concerning organic control policy cannot be made based on the brief benefit/cost assessment performed above. However, the following simple control policy does appear to have general merit in light of the above results. Since emission reductions according to reactivity based schemes are close to 90% for nearly all sources (for 90% overall control), organic control policy in Los Angeles should require large emission reductions for nearly all sources. Variations in degree of control among these sources should be dictated more by technical feasibility considerations than by reactivity considerations. Exceptions to this general rule should be made only for sources of extremely low reactivity. PCE drycleaning and 1,1,1-T degreasing now qualify as exceptions according to the reactivity classification schemes used in this report. By the use of substitutive controls, other source categories may qualify as exceptions in the future. These exceptions are likely to involve only sources which convert to synthetic solvents or gaseous fuels.

6.4 REFERENCES

1. "The Cost of Clean Air - Annual Report of the Administrator of the Environmental Protection Agency to the Congress of the United States in Compliance with Public Law 91-604, The Clean Air Act, as Amended", Document #93-40, 22-4470, 1973.

2. Private Communication, Ron Ketchum, Los Angeles County Air Pollution Control District, Los Angeles California, June 9, 1975.

APPENDIX A

COMPUTATION OF AVERAGE SOURCE MOLECULAR WEIGHTS

Tables A-1 through A-26 show the actual or estimated molecular weights of the compounds or groups of compounds emitted by the various emission sources. In the cases where sufficiently detailed data were available the actual molecular weights were determined either, in the case of a single compound, by recording the published molecular weights or, in the case of a group of compounds, by recording the appropriately weighted average molecular weight. Where composition estimates were required, the molecular weights were estimated by determining the molecular weight of an average compound. The average compound used was signified by the notation (C_n) where n is the number of carbon atoms in the molecule. In the case of halogenated compounds, the notation (C_nCl_m) was used where m is the number of chlorine atoms in the molecule.

The average molecular weight shown in each table was determined by calculating a weighted average based on the mole fraction of each type of compound as listed in the appropriate tables in Sections 3.2.1 and 3.4.5.

The following shows the tables which apply to each source type:

STATIONARY SOURCES -

FUELS AND COMBUSTION

Petroleum Production and Refining	Table
Petroleum Production	A-1
Petroleum Refining	A-2
Gasoline Marketing	
Underground Gasoline Tanks	A-3
Automobile Gasoline Filling	A-4
Fuel Combustion	A-5
Waste Burning and Other Fires	A-6

STATIONARY SOURCES - ORGANIC CHEMICALS

Table

- Surface Coating
  - Heat Treated A-7
  - Air Dried A-8
- Dry Cleaning
  - Petroleum Based Solvents A-9
  - Synthetic Solvents A-10
- Degreasing
  - TCE Solvent A-11
  - 1,1,1-T Solvent A-12
- Printing
  - Rotogravure A-13
  - Flexigraphic A-14
- Industrial Process Sources
  - Rubber and Plastic Manufacturing A-15
  - Pharmaceutical Manufacturing A-16
  - Miscellaneous Chemical Manufacturing A-17

MOBILE SOURCES

- Light Gasoline Powered Vehicles
  - Exhaust Emissions A-18
  - Evaporative Emissions A-19
- Heavy Duty Gasoline Powered Vehicles
  - Exhaust Emissions A-20
  - Evaporative Emissions A-21
- Other Gasoline Powered Equipment
  - Exhaust Emissions A-22
  - Evaporative Emissions A-23
- Diesel Powered Vehicles A-24
- Aircraft
  - Jet A-25
  - Piston A-26

TABLE A-7 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED BY PETROLEUM PRODUCING OPERATIONS

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	21	Mono-tert-alkyl benzenes		C_{4+}-paraffins	70	Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins	87	Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 29

TABLE A-2 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED BY PETROLEUM REFINERIES

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins (C_2)	30	Mono-tert-alkyl benzenes		C_{4+}-paraffins (C_7)	100	Prim-& sec-alkyl benzenes (C_8)	106	Aliphatic olefins (C_6)	84
Acetylene	26	Cyclic ketones		Cycloparaffins		Dialkyl benzenes (C_9)	120	α-methyl styrene	
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT **93**

TABLE A-3 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED FROM UNDERGROUND GASOLINE STORAGE TANKS

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	24	Mono-tert-alkyl benzenes		C_{4+}-paraffins	66	Prim-& sec-alkyl benzenes		Aliphatic olefins	64
Acetylene		Cyclic ketones		Cycloparaffins	70	Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 58

TABLE A-4 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED DUE TO AUTOMOBILE GASOLINE TANK FILLING

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	42	Mono-tert-alkyl benzenes		C_{4+}-paraffins	71	Prim-& sec-alkyl benzenes	56	Aliphatic olefins	71
Acetylene		Cyclic ketones		Cycloparaffins	72	Dialkyl benzenes	107	α-methyl styrene	
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	120
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT **74**

TABLE A-5 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED DURING FUEL COMBUSTION

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	18	Mono-tert-alkyl benzenes		C_{4+}-paraffins (C_6)	86	Prim-& sec-alkyl (C_9) benzenes	120	Aliphatic olefins (C_5)	70
Acetylene	26	Cyclic ketones		Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes(C_5)	86
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 25

TABLE A-6 ESTIMATED MOLECULAR WEIGHT OF THE ORGANICS EMITTED BY WASTE BURNING AND OTHER FIRES

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	17	Mono-tert-alkyl benzenes		C_{4+}-paraffins (C_6)	86	Prim-& sec-alkyl benzenes		Aliphatic olefins (C_5)	70
Acetylene	26	Cyclic ketones		Cycloparaffins		Dialkyl benzenes (C_9)	120	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes (C_4)	54	Branched alkyl ketones		Aliphatic aldehydes (C_5)	86
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl (C_4) alcohols	74	Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones (C_4)	72	Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol	32								
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 33

TABLE A-7 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED DURING HEAT TREATING OF SURFACE COATINGS

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins (C_2)	30	Mono-tert-alkyl benzenes		C_{4+}-paraffins (C_5)	72	Prim-& sec-alkyl benzenes (C_8)	106	Aliphatic olefins (C_4)	56
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes (C_9)	120	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 82

TABLE A-8 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED BY AIR DRIED SURFACE COATINGS

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{6+}-paraffins (C_6)	86	Prim-& sec-alkyl benzenes (C_8)	106	Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins (C_{10})	140	Dialkyl benzenes (C_9)	120	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones (C_6)	100	Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols (C_4)	74	Tri-& tetra-alkyl benzenes (C_{11})	148
Acetone	58			N-alkyl ketones (C_4)	72	Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates (C_5)	116	Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves (C_4)	90
Ethyl amines									
Dimethyl formamide									
Methanol	32								
Perhalogenated hydrocarbons									
Partially halogenated paraffins (C_2Cl_2)	90								

AVERAGE MOLECULAR WEIGHT **87**

TABLE A-9 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED FROM DRY CLEANING OPERATIONS USING PETROLEUM BASED SOLVENTS

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins (C_{11})	156	Prim-& sec-alkyl benzenes (C_8)	106	Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins (C_8)	114	Dialkyl benzenes (C_9)	120	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes (C_{11})	140
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT **126**

TABLE A-10 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED FROM DRY CLEANING OPERATIONS USING SYNTHETIC SOLVENTS

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins		Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons	166								
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 166

TABLE A-11 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED BY DEGREASING OPERATIONS USING TCE SOLVENT

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins		Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins	132	Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 132

TABLE A-12 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED BY DEGREASING OPERATIONS USING 1,1,1-T SOLVENT

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_2 paraffins		Mono tert-alkyl benzenes		C_{4+}-paraffins		Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins	134								

AVERAGE MOLECULAR WEIGHT 134

TABLE A-13 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED BY ROTOGRAVURE PRINTING

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins (C_6)	86	Prim-& sec-alkyl benzenes (C_8)	106	Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins (C_8)	112	Dialkyl benzenes (C_9)	120	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols (C_4)	74	Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates	125*	Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol	32								
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

* C_5 Acetates and other, C_7 esters in a two to one mole ratio.

AVERAGE MOLECULAR WEIGHT **82**

TABLE A-14 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED BY FLEXIGRAPHIC PRINTING

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins		Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols	58	Tri-& tetra-alkyl benzenes	
Acetone	58			N-alkyl ketones (C_4)	72	Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol	32								
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT $\boxed{57}$

TABLE A-15 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED DURING THE MANUFACTURE OF RUBBER, PLASTIC, PUTTY AND ADHESIVES

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins (C_6)	86	Prim-& sec-alkyl benzenes		Aliphatic olefins (C_8)	96
Acetylene		Cyclic ketones (C_6)	98	Cycloparaffins (C_7)	98	Dialkyl benzenes (C_9)	120	α-methyl styrene	132
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones (C_7)	114	Aliphatic aldehydes (C_3)	58
Benzaldehyde		2-nitropropane		Styrene	118	Prim-& sec-alkyl alcohols (C_5)	88	Tri-& tetra-alkyl benzenes	
Acetone	58			N-alkyl ketones (C_5)	86	Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols (C_5)	88			Prim-& sec-alkyl acetates (C_4)	72	Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins (C_2 Cl_2)	98								

AVERAGE MOLECULAR WEIGHT 73

TABLE A-16 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED DURING MANUFACTURING OF PHARMACEUTICALS

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins		Prim-& sec-alkyl benzenes		Aliphatic olefins	
Acetylene		Cyclic ketones (C_7)	112	Cycloparaffins		Dialkyl benzenes		α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones (C_7)	114	Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl (C_5) alcohols	88	Tri-& tetra-alkyl benzenes	
Acetone	58			N-alkyl ketones (C_5)	86	Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols (C_5)	88			Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol	32								
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT **75**

TABLE A-17 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED BY MISCELLANEOUS ORGANIC SOLVENT OPERATIONS

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins (C_7)	114	Prim-& sec-alkyl (C_8) benzenes	106	Aliphatic olefins (C_7)	112
Acetylene		Cyclic ketones		Cycloparaffins (C_7)	112	Dialkyl benzenes (C_9)	120	α-methyl styrene	
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl (C_6) ketones	100	Aliphatic aldehydes (C_5)	86
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl (C_5) alcohols	88	Tri-& tetra-alkyl (C_{10}) benzenes	134
Acetone	58			N-alkyl ketones (C_4)	72	Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols (C_5)	88			Prim-& sec-alkyl (C_6) acetates	116	Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers (C_5)	88
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol	32								
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT **80**

TABLE A-18 AVERAGE MOLECULAR WEIGHT OF THE ORGANIC EXHAUST EMISSIONS FROM LIGHT DUTY, GASOLINE POWERED VEHICLES

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	20	Mono-tert-alkyl benzenes		C_{4+}-paraffins	97	Prim-& sec-alkyl benzenes	92	Aliphatic olefins	[illegible]
Acetylene	26	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	113	α-methyl styrene	
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	123
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT **69**

TABLE A-19 AVERAGE MOLECULAR WEIGHT OF THE EVAPORATIVE EMISSIONS FROM LIGHT DUTY, GASOLINE POWERED VEHICLES

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	43	Mono-tert-alkyl benzenes		C_{4+}-paraffins	88	Prim-& sec-alkyl benzenes	92	Aliphatic olefins	82
Acetylene		Cyclic ketones		Cycloparaffins	70	Dialkyl benzenes	115	α-methyl styrene	
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	120
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 91

TABLE A-20 AVERAGE MOLECULAR WEIGHT OF THE ORGANIC EXHAUST EMISSIONS FROM HEAVY DUTY, GASOLINE POWERED VEHICLES

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	20	Mono-tert-alkyl benzenes		C_{4+}-paraffins	97	Prim-& sec-alkyl benzenes	92	Aliphatic olefins	40
Acetylene	26	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	113	α-methyl styrene	
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	123
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 69

TABLE A-21 AVERAGE MOLECULAR WEIGHT OF THE EVAPORATIVE EMISSIONS FROM HEAVY DUTY, GASOLINE POWERED VEHICLES

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	43	Mono-tert-alkyl benzenes		C_{4+}-paraffins	88	Prim-& sec-alkyl benzenes	92	Aliphatic olefins	82
Acetylene		Cyclic ketones		Cycloparaffins	70	Dialkyl benzenes	115	α-methyl styrene	
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	120
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 91

TABLE A-22 AVERAGE MOLECULAR WEIGHT OF THE ORGANIC EXHAUST EMISSIONS FROM OTHER TYPES OF GASOLINE POWERED EQUIPMENT

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	20	Mono-tert-alkyl benzenes		C_{4+}-paraffins	97	Prim-& sec-alkyl benzenes	92	Aliphatic olefins	60
Acetylene	26	Cyclic ketones		Cycloparaffins	110	Dialkyl benzenes	113	α-methyl styrene	
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	123
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT **69**

TABLE A-23 AVERAGE MOLECULAR WEIGHT OF THE EVAPORATIVE EMISSIONS FROM OTHER TYPES OF GASOLINE POWERED EQUIPMENT

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	43	Mono-tert-alkyl benzenes		C_{6+}-paraffins	88	Prim-& sec-alkyl benzenes	92	Aliphatic olefins	82
Acetylene		Cyclic ketones		Cycloparaffins	70	Dialkyl benzenes	115	α-methyl styrene	
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	120
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 91

TABLE A-24 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED IN DIESEL ENGINE EXHAUST

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	16	Mono-tert-alkyl benzenes		C_{4+}-paraffins	196	Prim-& sec-alkyl benzenes	125	Aliphatic olefins	47
Acetylene	26	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	191	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	58
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 89

TABLE A-25 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED IN JET ENGINE EXHAUST

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	30	Mono-tert-alkyl (C_{10}) benzenes	134	C_{4+}-paraffins (C_9)	128	Prim-& sec-alkyl (C_8) benzenes	106	Aliphatic olefins	112
Acetylene	26	Cyclic ketones		Cycloparaffins		Dialkyl benzenes (C_9)	120	α-methyl styrene	
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	128
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl (C_{11}) benzenes	148
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

TABLE A-26 AVERAGE MOLECULAR WEIGHT OF THE ORGANICS EMITTED IN PISTON ENGINE AIRCRAFT EXHAUST

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	20	Mono-tert-alkyl benzenes		C_{4+}-paraffins	97	Prim-& sec-alkyl benzenes	92	Aliphatic olefins	40
Acetylene	26	Cyclic ketones		Cycloparaffins	110	Dialkyl benzenes	113	α-methyl styrene	
Benzene	78	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	122
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									

AVERAGE MOLECULAR WEIGHT 56

APPENDIX B

ADDITIONAL SUPPORT DATA FOR COMPOSITION ESTIMATES

Tables B-1 through B-18 present additional documentation to support the composition data shown in Sections 3.2.1 through 3.4.5.

TABLE B-1 COMPOSITION OF THE VAPORS FROM UNDERGROUND GASOLINE STORAGE TANKS [1]

Compound	Mole % *	
	Vent Vapors from Regular Grade Gasoline Storage Tank	Vent Vapors from Premium Grade Gasoline Storage Tank
Methane	3.47	3.09
Ethane	1.93	1.66
Ethylene	0.37	0.63
Propane	0.90	0.56
Propylene	0.17	0.10
Isobutane	2.06	2.52
n-Butane	6.24	7.26
Isobutene Butene-1	0.37	0.32
trans-2-Butene	0.40	0.36
cis-2-Butene	0.31	0.32
3-Methyl 1-butene	3.22 } 6.43^{+}	2.93 } 5.86^{+}
Isopentane	3.21	2.93
n-Pentane	3.49	2.99
1-Pentene	0.32	0.24
2-Methyl 1-butene	0.63	0.49
2-Pentane	0.68	0.43
2,2-Dimethyl butane	0.28	0.29
2-Methyl 2-butene	1.00	0.74
2,3 Dimethyl butane 2-Methyl pentane	1.50	1.34
Cyclopentane	0.42	0.38
3-Methyl pentane	0.69	0.50
n-Hexane	0.55	0.46
2,4-Dimethyl pentane 2,3-Dimethyl pentane	0.08	0.14
n-Heptane		
Octene isomers	0.02	0.04
Benzene	0.01	0.01
Toluene	0.07	0.03
1,3-Dimethyl benzene 1,4-Dimethyl benzene	0.01	0.01

* Volume % assumed to equal mole % $^{+}$Approximately 50/50 split assumed.

TABLE B-2 COMPOSITION OF THE EQUILIBRIUM VAPORS ABOVE A LOS ANGELES AREA REGULAR GRADE GASOLINE - 80°F [1]

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	4	Mono-tert-alkyl benzenes		C_{4+}-paraffins	64	Prim-& sec-alkyl benzenes	2	Aliphatic olefins	26
Acetylene		Cyclic ketones		Cycloparaffins	2	Dialkyl benzenes	1	α-methyl styrene	
Benzene	1	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	5	TOTAL CLASS II	0	TOTAL CLASS III	66	TOTAL CLASS IV	3	TOTAL CLASS V	26

TABLE B-3 COMPOSITION OF THE EQUILIBRIUM VAPORS ABOVE A LOS ANGELES AREA REGULAR GRADE GASOLINE - 85°F [1]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	4	Mono-tert-alkyl benzenes		C_{4+}-paraffins	66	Prim-& sec-alkyl benzenes	1	Aliphatic olefins	26
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	1	α-methyl styrene	
Benzene	1	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	5	TOTAL CLASS II	0	TOTAL CLASS III	67	TOTAL CLASS IV	2	TOTAL CLASS V	26

TABLE B-4 COMPOSITION OF THE EQUILIBRIUM VAPORS ABOVE A LOS ANGELES AREA PREMIUM GRADE GASOLINE - 79°F [1]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	2	Mono-tert-alkyl benzenes		C_{4+}-paraffins	77	Prim-& sec-alkyl benzenes	3	Aliphatic olefins	15
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	1	α-methyl styrene	
Benzene	1	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	3	TOTAL CLASS II	0	TOTAL CLASS III	78	TOTAL CLASS IV	4	TOTAL CLASS V	15

TABLE B-5 COMPOSITION OF THE EQUILIBRIUM VAPORS ABOVE A LOS ANGELES AREA PREMIUM GRADE GASOLINE - 85°F [1]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	1	Mono-tert-alkyl benzenes		C_{6+}-paraffins	78	Prim-& sec-alkyl benzenes	3	Aliphatic olefins	15
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	1	α-methyl styrene	
Benzene	1	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	2	TOTAL CLASS II	0	TOTAL CLASS III	79	TOTAL CLASS IV	4	TOTAL CLASS V	15

TABLE B-6 COMPOSITION OF AVERAGE LOS ANGELES AREA GASOLINE VAPORS - 79-80°F [1]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	3	Mono-tert-alkyl benzenes		C_{4+}-paraffins	73	Prim-& sec-alkyl benzenes	3	Aliphatic olefins	18
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	1	α-methyl styrene	
Benzene	1	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	4	TOTAL CLASS II	0	TOTAL CLASS III	74	TOTAL CLASS IV	4	TOTAL CLASS V	18

Assuming 30 volume % regular grade gasoline and 70 volume % premium grade gasoline

TABLE B-7 COMPOSITION OF AVERAGE LOS ANGELES AREA GASOLINE VAPORS - 85°F [1]

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	2	Mono-tert-alkyl benzenes		C_{6+}-paraffins	75	Prim-& sec-alkyl benzenes	2	Aliphatic olefins	18
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	1	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	3	TOTAL CLASS II	0	TOTAL CLASS III	76	TOTAL CLASS IV	3	TOTAL CLASS V	18

Assuming 30 volume % regular grade gasoline and 70 volume % premium grade gasoline

TABLE B-8 COMPOSITION OF LOS ANGELES AREA GASOLINES [1]

Mole %*

Compound	Liquid Regular Grade Gasoline		Regular Grade Gasoline Vapors at 80°F		Regular Grade Gasoline Vapors at 85°		Liquid Premium Grade Gasoline		Premium Grade Gasoline Vapors at 79°F		Premium Grade Gasoline Vapors at 85°F	
Methane					0.07							
Ethane			0.36		0.28				0.02		0.01	
Ethylene			0.09		0.09				0.05		0.01	
Propane	0.02		0.39		0.54		0.01		0.36		0.17	
Propylene			0.08		0.08				0.03		0.02	
Isobutane	0.24		0.95		1.21		0.21		1.01		0.95	
n-Butane	1.72		3.46		4.59		3.10		4.02		3.95	
Isobutene 1-Butene	0.02		0.16		0.25		0.03		0.22		0.20	
Trans-2-butene	0.06		0.21		0.28		0.04		0.22		0.19	
Cis-2-butene	0.13		0.24		0.28		0.05		0.21		0.21	
3-Methyl Butene	3.71	7.43^{+}	1.84	3.69^{+}	2.50	5.00^{+}	3.67	7.34^{+}	1.70	3.40^{+}	1.82	3.64^{+}
Isopentane	3.72		1.85		2.50		3.67		1.70		1.82	
n-Pentane	4.74		2.14		2.89		3,83		1.66		1.97	
1-Pentene	0.32		0.20		0.25		0.18		0.16		0.23	
2-Methyl-1-butene	0.68		0.42		0.46		0.50		0.36		0.45	
Pentene	0.88		0.41		0.49		0.57		0.15		0.40	
2,2-Dimethyl butane	0.60		0.17		0.21		0.40		0.14		0.15	
2-Methyl-2-butene	1.48		0.86		1.04		1.03		0.70		0.83	
2,3 Dimethyl butane 2-Methyl pentane	6.09		0.96		1.32		5.13		1.01		0.98	
Cyclopentane	0.88		0.28		0.27		0.54		0.16		0.18	
3-Methyl pentane	3.57		0.52		0.68		2.48		0.50		0.45	
n-Hexane	3.96		0.50		0.66		2.90		0.48		0.46	
2,4 Dimethyl pentane	3.30		0.31		0.34		3.73		0.29		0.34	
2,5 Dimethyl pentane	4.51						5.24					
n-Heptane	2.30						1.88					
Iso-octane	10.0	12.2^{++}					10.0	11.1^{++}				
Octene isomers	2.2						1.1					
Octane Isomers	6.6	13.1^{+}	0.08		0.09		3.16	6.33^{+}	0.09		0.08	
Octene isomers	6.5						3.17					
n-Octane	0.30						0.38					
Benzene	6.92		0.12		0.18		3.77		0.21		0.19	
Toluene	6.11		0.32		0.30		9.58		0.39		0.36	
n-Nonane	0.13						0.12					
Ethyl benzene	1.23		0.01		0.01		1.58		0.02		0.02	
1,3 Dimethyl benzene 1,4 Dimethyl benzene	5.08		0.06		0.05		9.10		0.09		0.08	
1,2 Dimethyl benzene	1.83		0.02		0.02		3.43		0.02		0.02	
n-Propyl benzene	1.67						0.42					
1-Methyl-3 ethyl benzene 1-Methyl 4-ethyl benzene	2.46		0.01		0.01		3.53		0.01		0.01	
Tertiary butyl benzene	0.38	1.14^{++}					0.61	1.84^{++}	0.01		0.01	
1,3,5 Trimethyl benzene	0.38						0.61					
1-Methyl-2-ethyl benzene	0.38						0.62					
Secondary butyl benzene	0.79	2.37^{++}	0.01				1.35	2.76^{++}	0.01		0.01	
Isobutyl benzene	0.79				0.01		1.35					
1,2,4-Trimethyl benzene	0.79						1.36					
n-Butyl benzene	0.61	1.22^{+}					1.38	2.76^{+}				
1,2,3-Trimethyl benzene	0.61						1.38					
Other C-10 Aromatics	1.52						2.81					

* Volume % assumed to equal mole %

$^{+}$Approximately 50/50 split assumed.

$^{++}$Split assumed.

TABLE B-9 COMPOSITION OF A LOS ANGELES AREA REGULAR GRADE GASOLINE [1]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	7	Mono-tert-alkyl benzenes		C_{4+}-paraffins	53	Prim-& sec-alkyl benzenes	11	Aliphatic olefins	16
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	9	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	3
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	7	TOTAL CLASS II	0	TOTAL CLASS III	54	TOTAL CLASS IV	20	TOTAL CLASS V	19

TABLE B-10 COMPOSITION OF A LOS ANGELES AREA PREMIUM GRADE GASOLINE [1]

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{6+}-paraffins	47	Prim-& sec-alkyl benzenes	15	Aliphatic olefins	9
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	19	α-methyl styrene	
Benzene	4	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	5
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	4	TOTAL CLASS II	0	TOTAL CLASS III	48	TOTAL CLASS IV	34	TOTAL CLASS V	14

TABLE B-11 COMPOSITION OF AVERAGE LOS ANGELES AREA GASOLINE [1]

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins		Mono-tert-alkyl benzenes		C_{4+}-paraffins	49	Prim-& sec-alkyl benzenes	14	Aliphatic olefins	11
Acetylene		Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	16	α-methyl styrene	
Benzene	5	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	4
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	5	TOTAL CLASS II	0	TOTAL CLASS III	50	TOTAL CLASS IV	30	TOTAL CLASS V	15

Assuming 30 volume % regular grade gasoline and 70 volume % premium grade gasoline

TABLE B-12 ESTIMATED COMPOSITION OF THE ORGANICS EMITTED AS AUTOMOBILE EXHAUST - UNCONTROLLED [2]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	20	Mono-tert-alkyl benzenes		C_{4+}-paraffins	22	Prim-& sec-alkyl benzenes	6	Aliphatic olefins	31
Acetylene	12	Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	4	α-methyl styrene	
Benzene	2	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	2
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	34	TOTAL CLASS II	0	TOTAL CLASS III	23	TOTAL CLASS IV	10	TOTAL CLASS V	33

TABLE B-13 COMPOSITION OF THE ORGANICS EMITTED AS AUTOMOBILE EXHAUST - MODIFIED COMBUSTION [2]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	19	Mono-tert-alkyl benzenes		C_{4+}-paraffins	15	Prim-& sec-alkyl benzenes	5	Aliphatic olefins	61
Acetylene	11	Cyclic ketones		Cycloparaffins	1	Dialkyl benzenes	4	α-methyl styrene	
Benzene	2	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	2
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	32	TOTAL CLASS II	0	TOTAL CLASS III	16	TOTAL CLASS IV	9	TOTAL CLASS V	63

Modified combustion consists of lean mixture and modified spark timing.

TABLE B-14 COMPOSITION OF THE ORGANICS EMITTED AS AUTOMOBILE EXHAUST - AIR INJECTION [2]

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	17	Mono-tert-alkyl benzenes		C_{4+}-paraffins	18	Prim-& sec-alkyl benzenes	5	Aliphatic olefins	40
Acetylene	9	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	4	α-methyl styrene	
Benzene	2	Tert-alkyl acetates		Alkyl acetylenes	1	Branched alkyl ketones		Aliphatic aldehydes	
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	4
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	28	TOTAL CLASS II	0	TOTAL CLASS III	19	TOTAL CLASS IV	9	TOTAL CLASS V	44

TABLE B-15 COMPOSITION OF AUTOMOBILE EXHAUST HYDROCARBON EMISSIONS IN AN ENCLOSED AREA [3]

Compound	Molecular Weight	Weight % Sepulveda Blvd. Tunnel	Weight % 2nd Street Tunnel	Weight % Average	Mole %
Ethane	30	1.5 ± 0.35	1.2 ± 0.10	1.4 ± 0.31	3.3
Ethylene	28	7.0 ± 0.71	4.4 ± 0.43	6.3 ± 1.4	13.8
Acetylene	26	5.0 ± 0.60	3.9 ± 0.58	4.7 ± 0.80	12.7
Propane	44	1.0 ± 0.08	1.0 ± 0.13	1.0 ± 0.71	1.6
Propylene	42	3.2 ± 0.33	2.0 ± 0.18	2.8 ± 0.61	4.7
Isobutane	58	0.8 ± 0.16	0.9 ± 0.06	0.8 ± 0.14	1.0
Butane	58	2.5 ± 0.37	2.5 ± 0.15	2.5 ± 0.31	3.0
Isopentane	72	5.4 ± 0.38	5.9 ± 0.49	5.5 ± 0.46	5.2
Pentane	72	2.8 ± 0.24	3.0 ± 0.24	2.9 ± 0.24	2.8
2-Methyl Pentane + 2,3-Dimethyl Pentane	93	2.2 ± 0.24	3.3 ± 0.20	2.5 ± 0.61	1.9
3-Methyl Pentane	86	3.3 ± 0.25	3.6 ± 0.33	3.4 ± 0.31	2.8
C_6 Olefins	84	1.7 ± 0.13	1.9 ± 0.14	1.7 ± 0.16	1.4
Hexane	86	1.9 ± 0.18	2.2 ± 0.14	2.0 ± 0.22	1.6
Methyl cyclopentane	84	---	---	---	---
2,4-Dimethyl Pentane	100	2.0 ± 0.16	2.1 ± 0.13	2.0 ± 0.17	1.4
Benzene	78	3.4 ± 0.16	2.7 ± 0.22	3.2 ± 0.38	2.9
2,3-Dimethyl Pentane	100	1.9 ± 0.14	1.9 ± 0.08	1.9 ± 0.12	1.3
3-Methyl Hexane	100	1.3 ± 0.09	1.4 ± 0.10	1.3 ± 0.10	0.9
2,2,4-Trimethyl Pentane	114	2.2 ± 0.16	2.3 ± 0.08	2.2 ± 0.16	1.3
Heptane	100	1.4 ± 0.10	1.3 ± 0.10	1.3 ± 0.09	0.9
Methyl cyclohexane	98	0.9 ± 0.06	0.9 ± 0.10	0.9 ± 0.07	0.6
Isooctane	114	1.0 ± 0.07	1.0 ± 0.06	1.0 ± 0.07	0.6
Toluene	92	9.2 ± 1.03	8.6 ± 0.22	9.0 ± 0.90	6.9
Dimethyl Hexanes methyl Heptane	114	1.5 ± 0.49	1.9 ± 0.61	1.6 ± 0.54	1.0
Octane	114	1.8 ± 0.28	1.9 ± 0.10	1.8 ± 0.20	1.1
Dimethyl Heptane + Methyl Octanes	128	1.2 ± 0.09	1.3 ± 0.00	1.2 ± 0.09	0.6
meta-and para-Xylenes	106	9.4 ± 0.54	9.5 ± 0.42	9.5 ± 0.48	6.3
ortho-Xylene	106	4.1 ± 0.17	4.2 ± 0.13	4.1 ± 0.16	2.7
Nonane	128	0.9 ± 0.10	1.1 ± 0.13	1.0 ± 0.13	0.6
2,4,5-Trimethy Octane	156	0.7 ± 0.12	0.8 ± 0.08	0.7 ± 0.10	0.4
Isodecane	142	0.3 ± 0.25	0.0 ± 0.00	0.2 ± 0.22	0.1
3-and 4-Ethyl Toluene	142	6.8 ± 0.48	7.7 ± 0.75	7.1 ± 0.60	3.5
Decane	142	5.0 ± 0.51	5.5 ± 0.70	5.3 ± 0.59	2.6
1,2,4-Trimethyl Benzene	120	1.5 ± 0.38	1.6 ± 0.31	1.5 ± 0.33	0.9
1,2,3-Trimethyl Benzene	120	1.0 ± 0.31	1.2 ± 0.34	1.0 ± 0.30	0.6
3-Propyl Toluene	134	2.3 ± 0.75	2.7 ± 0.67	2.4 ± 0.70	1.3
C_4 Benzenes	134	2.4 ± 1.66	2.7 ± 1.47	2.4 ± 1.58	1.3
		100.3 %	100.7 %	100.6 %	
Methane [4]					10.0*

*Approximately 10.0 mole % of the organic compounds emitted in automobile exhaust is methane; methane was not measured at the same time as the compounds shown above.

TABLE b-16 ESTIMATED COMPOSITION OF THE ORGANICS EMITTED IN GAS TURBINE EXHAUST - TAXI-IDLE MODE [5]

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	7	Mono-tert-alkyl benzenes	4	C_{4+}-paraffins	22	Prim-& sec-alkyl benzenes	16	Aliphatic olefins	20
Acetylene	1	Cyclic ketones		Cycloparaffins		Dialkyl benzenes	15	α-methyl styrene	
Benzene	1	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	10
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	4
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	9	TOTAL CLASS II	4	TOTAL CLASS III	22	TOTAL CLASS IV	31	TOTAL CLASS V	34

TABLE B-17 ESTIMATED COMPOSITION OF THE ORGANICS EMITTED IN GAS TURBINE EXHAUST - TAKEOFF MODE [5]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	2	Mono-tert-alkyl benzenes	6	C_{4+}-paraffins	15	Prim-& sec-alkyl benzenes	8	Aliphatic olefins	20
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes	13	α-methyl styrene	
Benzene		Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	30
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	6
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	2	TOTAL CLASS II	6	TOTAL CLASS III	15	TOTAL CLASS IV	21	TOTAL CLASS V	56

TABLE B-18 ESTIMATED COMPOSITION OF THE ORGANICS EMITTED IN GAS TURBINE EXHAUST - APPROACH MODE [5]

MOLE %

CLASS I		CLASS II		CLASS III		CLASS IV		CLASS V	
C_1-C_3 paraffins	1	Mono-tert-alkyl benzenes		C_{4+}-paraffins	10	Prim-& sec-alkyl benzenes	9	Aliphatic olefins	10
Acetylene		Cyclic ketones		Cycloparaffins		Dialkyl benzenes	9	α-methyl styrene	
Benzene	1	Tert-alkyl acetates		Alkyl acetylenes		Branched alkyl ketones		Aliphatic aldehydes	60
Benzaldehyde		2-nitropropane		Styrene		Prim-& sec-alkyl alcohols		Tri-& tetra-alkyl benzenes	
Acetone				N-alkyl ketones		Cellosolve acetate		Unsaturated ketones	
Tert-alkyl alcohols				Prim-& sec-alkyl acetates		Partially halogenated olefins		Diacetone alcohol	
Phenyl acetate				N-methyl pyrrolidone				Ethers	
Methyl benzoate				N,N-dimethyl acetamide				Cellosolves	
Ethyl amines									
Dimethyl formamide									
Methanol									
Perhalogenated hydrocarbons									
Partially halogenated paraffins									
TOTAL CLASS I	2	TOTAL CLASS II	0	TOTAL CLASS III	10	TOTAL CLASS IV	18	TOTAL CLASS V	70

References

1. Private Communication, Los Angeles County Air Pollution Control District, November 1974, Internal Document Titled "Liquid and Equilibrium Vapor Analysis (APCD) - Test No. C-1840," August 9, 1972.

2. W. E. Morris and K. T. Dishart, "Influence of Vehicle Emission Control Systems on the Relationship Between Gasoline and Vehicle Exhaust Hydrocarbon Composition," Effect of Automotive Emission Requirements on Gasoline Characteristics, ASTM STP 487, American Society for Testing and Materials, 1971, pp. 63-101.

3. Private Communication, Henry Mayerson, California Air Resources Board, El Monte, California, November 1974; Results of Tests of Automotive Hydrocarbon Emissions in Two Long Highway Tunnels.

4. Private Communication, Henry Mayerson, California Air Resources Board, El Monte, California, January 1975.

5. J. O. Chase and R. W. Hurn, "Measuring Gaseous Emissions From An Aircraft Turbine Engine," SAE #700249, presented at the Society of Automotive Engineers National Air Transportation Meeting, New York, April 20-23, 1970.